Flexible Micro-Supercapacitor Based on Pen Ink-Carbon Fiber Thread

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Complete List of Authors:	Dai, Shuge; Chongqing University, Department of Applied Physics Guo, Hengyu; Chongqing University, Applied Physics Wang, Mingjun; Chongqing University, Applied physics Liu, Jianlin; Chongqing University, Applied Physics Wang, Guo; Chongqing University, Department of Applied Physics Hu, Chenguo; Chongqing University, Applied Physics Xi, Y; Chongqing University, Applied Physics

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Flexible Micro-Supercapacitor Based on Pen Ink-Carbon Fiber Thread

Shuge Dai, Hengyu Guo, Mingjun Wang, Jianlin Liu, Guo Wang, Chenguo Hu*, Yi Xi*

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A highly flexible solid-state micro-supercapacitor based on Pen Ink-carbon-fiber (Ink-CF) thread structure was fabricated with excellent electrochemical performance such as high capacitance of 4.31 mF cm^{-2}, and an energy density of 3.8×10^{-7} Wh cm^{-2} at a power density of 5.6×10^{-6} W cm^{-2}. This fabricated structure shows excellent characteristics such as lightweight, small volume, flexibility and portability. By integrating it with a triboelectric nanogenarator, the micro-supercapacitors could be charged and power 8 commercial LEDs, demonstrating its feasibility as an efficient storage component and self-powered micro/nanosystems.

Introduction

Recently, flexible energy storage devices have attracted great attention in many emerging wearable or rolling-up modern gadgets, such as roll-up displays, sensor networks and other personal multimedia devices. [1, 2] Among various types of energy storage devices, a supercapacitor is a very attractive alternative to batteries, owing to its many promising features such as high power density, fast charge-discharge rates, and long cycle life.[3-6] Compared with the conventional planar structure, a wire device has many advantages such as high flexibility, lightweight, moreover, it can easily be woven into textiles or other structures and exhibit unique and promising applications.[7] This kind of the wire-shaped supercapacitors could be woven into any shape and placed anywhere.[8] Meanwhile, wire-shaped architecture can remove traditional restriction and meet the requirements of wearable energy storage devices and thus open up a path for design innovation.[9, 10] However, it remains a great challenge to obtain wire-shaped supercapacitors with high performance.

In general, a suitable electrode material is required to fabricate wire-shaped devices. Recently, carbon nanotubes (CNTs) have been widely used as electrode materials in conventional planar energy storage systems.[11,12] In general, active materials are usually used as electrode materials such as activated carbon, carbon nanotubes and graphene because of the high specific surface area of these materials, which make them suitable for reversible ion adsorption or charge storage.[10,13-15] Although carbon materials are abundant and electrochemically stable, their relatively high internal series resistance, limited surface area accessible to the electrolyte ions, and pore morphology requirements restrict the capacitance performance of carbon-based supercapacitors.[10] Such as CNTs, its electrical double-layer capacitance is limited, meanwhile, CNTs are generally made in a network format that the charges produced have to cross many boundaries with low efficient transmission.[7, 16] Hence, it is a great challenge to develop novel carboneous electrode materials with great electrochemical performance for supercapacitors.

Herein, we report a novel high-performance wire-shaped all-solid-state micro-supercapacitor based on Pen Ink-carbon-fiber (Ink-CF) thread nanostructure, the CF serves as a scaffold and current collector, and the Ink is coated on the surface of the CF thread by a simple dip-coating process.[8, 17] The CF can be used as a good scaffold to load active materials and to fabricate flexible, lightweight, small and wearable supercapacitors due to its high conductivity, large surface areas, and small size.[18] The simple dip-coating method can be used to form a uniform film on the fibrous substrates, meanwhile, the Ink coating makes these CF threads (with a diameter of about 0.6 mm) highly conductive without affecting theirs shape. Commercial pen ink exhibits great dispersion and strong adhesion. Compared with numerous existing carbon materials, pen ink has many advantages such as high stability, low cost, and well-established industrial production.[10] The solid-state electrolyte (LiCl-PVA) is chosen for the micro-supercapacitors because it will overcome the major drawbacks of conventional liquid electrolytes. For instance, leakage problem of electrolyte in device integration and environment friendliness are very crucial for the development of flexible, lightweight and portable electronics.[19] The device demonstrates the highest areal specific capacitance of 4.31 mF cm^{-2}, and length specific capacitance of 0.258 mF cm^{-1} at a current of 0.005 mA. It also shows excellent long-term cycling stability and flexibility. Furthermore, the micro-supercapacitors integrated with a triboelectric nanogenerator can power 8 light-emitting-diodes (LEDs), which displays potential applications for self-powered micro/nanosystems.

Experimental Section

Preparation of materials and devices

Carbon fiber threads (Shanghai Lishuo Composite Material Technology Company) and the pen ink (from Hero, Shanghai Ink Factory in China) were used here as purchased. In the fabrication process for the Ink-CF thread, firstly, the carbon fiber threads which were cleaned by acetone, ethanol and deionized water for several times were dipped into the Pen ink. The CF threads would be well coated by ink due to its strong adsorption and strong adhesion.[10] Then the carbon fiber threads with well coated ink were subsequently dried in oven at 60℃ for about 30 min. In addition, the resistance of the carbon fiber threads was measured before and after being coated with ink. This process was repeated many times until the sample with needed mass loading of graphite was achieved, and the density of the mass loading is about 0.48 mg cm^{-1}.(Pen ink is mainly composed of graphite) Through this repeated dipping and drying process, a highly conductive Ink-CF thread was achieved.[8] The Ink-CF thread was measured to be 10 Ω cm^{-1}.

Fabrication of solid-state micro-supercapacitor

Firstly, one Ink-CF thread was textile-wrapped around a plastic wire (with a diameter of about 1.2 mm) as an internal electrode with about 2 cm in length. Secondly, the electrode was coated with a layer of electrolyte (LiCl-PVA gel), and was wrapped with a separator (Whatman 8 μm filter paper) which was coated with electrolyte on both sides. Finally, another Ink-CF thread was textile-wrapped around the separator with about 2 cm in length as an outer electrode for the micro-supercapacitor.

Preparation of the nanogenerator

The fabrication of the triboelectric nanogenerator was reported in literature.[20]

Characterization and the electrochemical measurement

The morphology, chemical composition, and the structure of the products were characterized by field-emission scanning electronmicroscopy (Nova 400 Nano SEM). Raman spectrometer investigations were performed by using Witec Confocal Raman microscopy (Lab RAM HR Evolution). The CV and galvanic charge-discharge measurement was conducted with an electrochemical workstation (CHI760D). I-V curve was measured through a low-noise preamplifier system (Keithley 4200). A Stanford Low-noise Current Preamplifier (Model SR570) and a Data Acquisition Card (NI PCI-6259) were used to measure the voltage-time curve of the device.

Results and discussion

Fig. 1a and b show SEM images of the microstructure of the CF thread. The image reveals the diameter of a bundle of CFs is about 0.5 mm. Fig. 1c, d and e. show SEM images of the Ink-CF thread after being coated with the ink. The enlarged Ink-CF surface clearly displays that the pen ink forms a relatively uniform film on the surface of the CF substrate (Fig. 1d), and higher resolution SEM images of the pure CF and Ink-CF are presented in Fig. S1. The cross-section of the pure CF and Ink-CF is shown in Fig. S2, which clearly indicates a strong adhesiveness between the CF and coated Ink layer. SEM image at high magnification (Fig. 1e) reveals that the ink film consists of nanoparticles that bond together to form a porous morphology. Such porous morphology is beneficial to the adsorption of electrolyte ions.[10] Raman spectra of the Pen ink (Fig. 1f) verifies that the active component in pen ink is mainly graphite carbon nanoparticles. As is shown in Fig. 1f, the G and D peaks are clearly observed at 1355 cm^{-1} (attributed to the disordered carbonaceous component) and 1585 cm^{-1} (attributed to the ordered graphitic component), respectively, which are consistent with the literature reported.[19] The Raman spectrum for the pure CF and the Ink-CF composite are also measured and presented in Fig. S3. As is shown in Fig.S4, the I-V plot shows that the Ink-CF thread has a high conductivity after being well coated with the ink with resistance of 10 Ω cm^{-1}, which is less than the bare CF thread with resistance of 12 Ω cm^{-1}. The enhance conductivity may be due to a considerable number of graphite crystallites exist in the ink carbon layer on the CF.

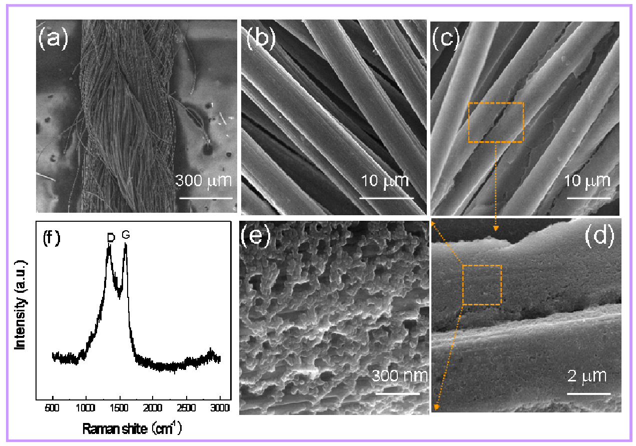

Fig. 1. SEM images of the pure CF thread (a-b), the Ink-CF thread (c), the enlarged Ink-CF surface (d-e) and Raman spectra of the Pen Ink (f).

The optical photograph of the steps of the fabrication of the Ink-CF wire-shaped all-solid-state micro-supercapacitor is shown in Fig. 2a. The top photograph shows the structure of plastic wire, the middle photograph presents the morphology and size of the first layer of Ink-CF thread textile-wrapped, and the bottom photograph presents the final fabricated Ink-CF wire-shaped all-solid-state micro-supercapacitor. Fig. 2b shows the cyclic voltammetry (CV) curves of the bare CF and Ink-CF thread devices at a scan rate of 100 mV s^{-1}, which display excellent electrochemical performance of the Ink-CF electrodes. Fig. 2c gives the CV curves of the Ink-CF electrodes at different scan rates with potential windows ranging from 0 to 0.8 V. The CV curves for the bare CF thread device at various scan rates are also achieved and displayed in Fig. S5a. All the CV curves retain their nearly rectangular shapes with slight variations even at a scan rate of 1 V s^{-1}, revealing excellent capacitive behaviors of the Ink-CF electrodes. Compared with the bare CF thread device, the areal special capacitance of the Ink-CF electrodes is higher with about 3.5 mF cm^{-2} at a scan rate of 10 mV s^{-1} and the results are shown in Fig. 2d. Owing to the large surface areas, great electronic conductivity and high stability of graphite, the capacitance of the CF electrodes is greatly improved by coating with Ink. In addition, a large number of porous, which the graphite carbon

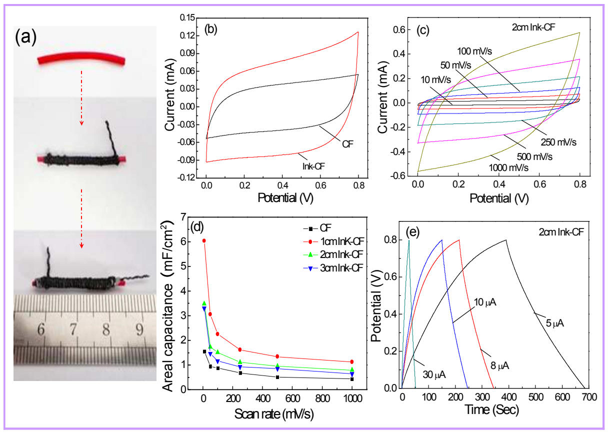

Fig. 2 (a) Optical photographs of the steps of the fabrication of the Ink-CF wire-shaped all-solid-state micro-supercapacitor. (b) CV curves of bare CF and Ink-CF thread devices at a scan rate of 100 mV s^{-1}. (c) CV curves of the Ink-CF (about 2cm) thread device at different scan rates. (d) The specific capacitances of the micro-supercapacitors with different structures at various scan rates. (e) Galvanostatic charge-discharge curves of the Ink-CF thread device (about 2 cm) at various current.

nanoparticles bond together to form on the surface of the CF, enhance the electrochemical adsorption of electrolyte ions. Fig. 2e shows the Galvanostatic charge-discharge curves of the Ink-V, which display good linear voltage-time profiles with small IR drops, and all the charging curves are nearly symmetrical with their similar discharge counterparts, indicating the high power output of the Ink-CF micro-supercapacitor.

The effect of winding length on the capacitance of the Ink-CF electrodes is also explored. The CV curves of the Ink-CF electrodes at various scan rates with different lengths (about 1cm, 3cm) are displayed in Fig. S5b and c. The shapes of these CV curves does not significantly change even at an ultrafast scan rate, revealing the ideal electrochemical performance of the Ink-CF electrode structure, meanwhile, the areal specific capacitance is also calculated as is shown in Fig. 2d. The special capacitance decreases with the increasing in the winding length of the Ink-CF electrode. The reason is that the internal resistance of the micro-supercapacitor increases with the increase in winding length, which may hinder the ionic and electronic transport through the electrode system. Galvanostatic charge-discharge curves of the micro-supercapacitors with different structures collected in a stable potential window of 0-0.8 V at a fixed current of 30 μA are shown in Fig. 3a. The discharge curves are almost symmetrical to the corresponding charge curves, revealing good electrochemical capacitance behavior of the micro-supercapacitors. Galvanostatic charge-discharge curves of the Ink-CF electrodes (about 1 cm) at various currents are displayed in Fig. 3b. Galvanostatic charge-discharge curves of the bare CF electrodes were also collected and shown in Fig.S5d. All these curves present a nearly typical symmetrical triangular shape, further verifying the excellent capacitive behavior of the Ink-CF micro-supercapacitors. The special capacitance of the bare CF and Ink-CF (about 1 cm and 2 cm) thread devices at various charge-discharge currents are shown in Fig. 3c. The areal special capacitance was calculated as the following equation

$$Cs = \frac{I\Delta t}{S\Delta V} \qquad (1)$$

where I, ΔV, Δt, and S are the discharge current, the potential window during the discharge process (the IR drop), the discharge time and the effective area of the electrode respectively. The highest special capacitance of the Ink-CF electrodes is 4.3 mF cm^{-2} (the length capacitance 0.258 mF cm^{-1}) at a current of 5 μA, which is higher than the values reported for micro-supercapacitors (0.4-2 mF cm^{-2}).[1, 21-23] Energy density (E) and power density (P) are two important parameters for evaluating the electrochemical behavior of the supercapacitors,[24] which are calculated as

$$E = \frac{CV^2}{2S} \qquad (2)$$

$$P = \frac{E}{t} \qquad (3)$$

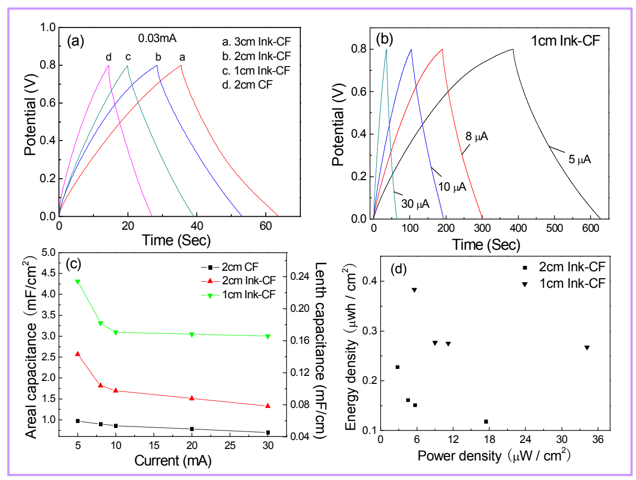

Fig. 3 (a) Galvanostatic charge-discharge curves of CF, Ink-CF thread devices with different lengths at a current of 30 μA. (b) Galvanostatic charge-discharge curves of the Ink-CF thread device (about 1cm) at various currents. (c) The special capacitances of bare CF and Ink-CF (about 1 cm and 2 cm) thread devices at various charge-discharge currents. (d) Ragone plots of the Ink-CF thread devices (about 1 cm and 2 cm).

where C, V, S and t are the total capacitance of the device, cell voltage, effective area of the electrode and discharge time, respectively. The Ragone plots of the Ink-CF thread devices (about 1 cm and 2 cm) are displayed in Fig. 3d.

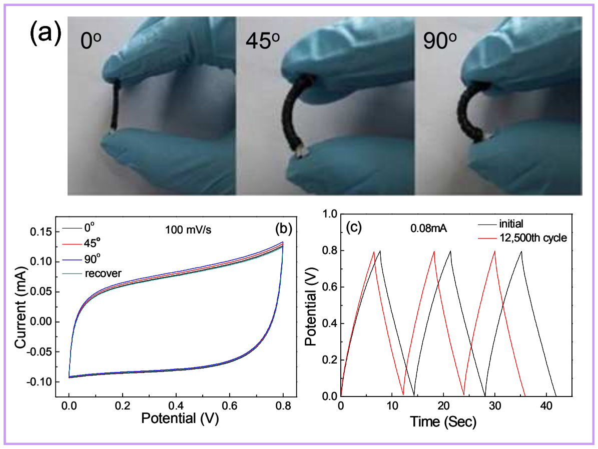

Fig. 4 (a) Photographs of Ink-CF (about 2 cm) micro-supercapacitor bended with different angles. (b) CV curves of Ink-CF (about 2 cm) micro-supercapacitor at various bending states. (c) Cycle life. The inset was the galvanostatic charge-discharge curves at a current of 0.08 mA of the Ink-CF thread device (about 2 cm) before and after long-term cycling.

The power density and energy density of the Ink-CF electrodes are 0.3-3.4×10^{-5} W cm^{-2} and 1.2-3.8×10^{-7} Wh cm^{-2}, which are comparable to those reported GF@3D-G supercapacitor (Power density: 6-100×10^{-6} W cm^{-2}, energy density 0.4-1.7×10^{-7} Wh cm^{-2}),[25] and ZnO nanowire-based fiber supercapacitor (Power density: 1.4×10^{-5} W cm^{-2}, energy density: 2.7×10^{-8} Wh cm^{-2}).[1] For practical application consideration, flexible and portable electronics are highly desired. As is shown in Fig. 4a, the Ink-CF micro-supercapacitor (about 2 cm) is highly flexible and lightweight and even can be twisted without destroying its construction. Moreover, the CV curves are not significantly changed under different bending angles, revealing its well flexibility (Fig. 4b). In addition, the Ink-CF micro-supercapacitor displays a long-term cycling stability between 0 and 0.8 V at a current of 0.08 mA and keeps at 87.4% of its initial capacitance after 12500 charge-discharge cycles (Fig. 4c). Moreover, the discharge curves remain symmetric with charging counterparts and display good linear voltage-time profiles after 12500 times, which demonstrates its excellent long-term cycling stability.

As efficient energy storage devices, supercapacitors can not only be charged and then discharged to drive different electronic devices but also can store energy from various other energy sources, especially sustainable and renewable energy sources from ambient.[16, 26] Therefore, to demonstrate the potential applications of our novel fabricated micro-supercapacitors, a simple self-powered system module is designed as is shown in Fig. 5a. The optical photograph and schematic diagram of the triboelectric nanogenerator are displayed in Fig. 5b. The triboelectric nanogenerator here is used to harvest mechanical energy by contacting and separating the PTFE film and Al electrode under a periodic compressive force by an electric oscillator at a frequency of 10 Hz.[27] To enable the micro-supercapacitors to be charged continually, the output electric signals are first rectified by a bridge rectifier, which transforms alternating current (AC) to direct current (DC).[18] Three micro-supercapacitors connected in series can power 8 light emitting diodes (LEDs) well for about 1 min after being charged to 3.5 V by the triboelectric nanogenerator as is shown in Fig. 5c (for detail information, see Fig. S6). Fig. 5d shows the charging curve of three micro-supercapacitors connected in series, from which we can see that these micro-supercapacitors can be charged to 3.5 V within 4 min by the triboelectric nanogenerator, demonstrating fast and good energy storage.

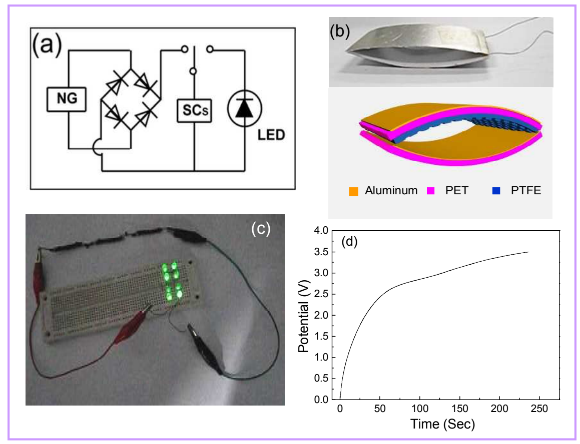

Fig. 5 (a) Schematic diagram of the self-powered nanosystem which is integrated by a triboelectric nanogenerator and three micro-supercapacitors (2 cm each). (b) Optical photograph (top) and schematic diagram of the triboelectric nanogenerator (bottom). (c) Optical photograph of 8 commercialized LEDs lighted by charged micro-supercapacitors connected in series. (d) Charging curve of three micro-supercapacitors connected in series charged by the triboelectric nanogenerator.

Conclusions

In summary, we have designed and fabricated highly flexible all-solid-state micro-supercapacitors based on Ink-CF threads. The micro-supercapacitors show excellent electrochemical performance such as high power density of 3.8×10^{-7} Wh cm^{-2}, high specific capacitance of 4.31 mF cm^{-2} at a current of 5 μA, and good cycling stability. Moreover, the micro-supercapacitors could be charged and then power 8 commercial LEDs well for about 1 min after being charged to 3.5 V by integration with a triboelectric nanogenarator, demonstrating its potential application in self-powered nanotechnology, which also opens up a new path for the preparation of flexible micro-supercapacitors.

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Notes and references

*Department of Applied Physics, Chongqing University,Chongqing, 400044, P.R. China, *Corresponding author. Tel: +86 23 65678362; Fax: +86 23 65678362; E-mail addressed: hucg@cqu.edu.cn (CG Hu); yxi6@cqu.edu.cn (Y Xi)*

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Graphical abstract

A highly flexible solid-state micro-supercapacitor based on Pen Ink-carbon-fiber (Ink-CF) thread structure is fabricated with excellent electrochemical performance and advantages of lightweight, small volume, flexibility and portability. By integration with a triboelectric nanogenarator, the micro-supercapacitors are charged and used to power commercial LEDs, demonstrating its feasibility as an efficient storage component for self-powered micro/nanosystems.