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A knittable fiber-shaped supercapacitor based on natural cotton thread for wearable electronics

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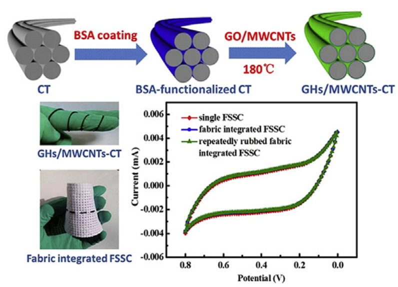
HIGHLIGHTS

- Natural cotton thread is used as skeleton to fabricate flexible electrode materials.
- Fiber shaped electrode is prepared through a one-step hydrothermal process.
- All-solid fiber-shaped supercapacitor achieves good capacitive performance.
- The fabric integrated fiber-shaped supercapacitor also shows stable performance.

GRAPHICAL ABSTRACT



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ABSTRACT

At present, the topic of building high-performance, miniaturized and mechanically flexible energy storage modules which can be directly integrated into textile based wearable electronics is a hotspot in the wearable technology field. In this paper, we reported a highly flexible fiber-shaped electrode fabricated through a one-step convenient hydrothermal process. The prepared graphene hydrogels/multi-walled carbon nanotubes-cotton thread derived from natural cotton thread is electrochemically active and mechanically strong. Fiber-shaped supercapacitor based on the prepared fiber electrodes and polyvinyl alcohol-H_3PO_4 gel electrolyte exhibits good capacitive performance (97.73 μF cm^{-1} at scan rate of 2 mV s^{-1}), long cycle life (95.51% capacitance retention after 8000 charge-discharge cycles) and considerable stability (90.75% capacitance retention after 500 continuous bending cycles). Due to its good mechanical and electrochemical properties, the graphene hydrogels/multi-walled carbon nanotubes-cotton thread based all-solid fiber-shaped supercapacitor can be directly knitted into fabrics and maintain its original capacitive performance. Such a low-cost textile thread based versatile energy storage device may hold great potential for future wearable electronics applications.

1. Introduction

With the constantly increasing demand for more portable and intelligent electronic products, wearable electronics have aroused considerable attention in the recent years. Indeed, it has been forecasted that the field of wearable technology is posed to explode in the next ten years [1]. For instance, smart garments, which are fabricated by implanting various functional electronic components (e.g. textile energy harvesting/storage systems, sensor fabrics, communication components and integrated textile circuitries) into daily clothing, are typical sort of wearable electronics with

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enormous perspectives for development [2–4]. The potential applications for smart garments are attractive and tremendous, such as wearable display, medical monitor, high-performance sportswear and military equipment [5]. Currently, researchers are dedicated in incorporating modes of actuation and communication directly into wearable textiles to construct multiple smart garments with typical functionalities. In general, producing fully integrated energy storage system (such as fiber-shaped batteries and supercapacitors) which is the primary component of garments devices is a prerequisite for constructing self-powered smart garments [6]. Therefore, building high-performance and fully integrated energy storage systems is rather urgent since conventional capacitors and batteries are too heavy and bulky for wearable electronics [7–9]. As an emerging type of flexible energy storage device, fiber-shaped supercapacitor (FSSC) is capable of being knitted into textiles directly without deteriorating their original comfortable sensation. Therefore, with the rapid development of wearable electronics, FSSCs have attracted significant interest as an innovative power supply device among the researchers.

The common research target on FSSC is to develop devices in the form of fully integratable fibers while preserving their capacitance comparable to conventional supercapacitors [10]. To date, the flourishing research on FSSCs has made significant progress in fabricating fiber-shaped electrodes. Firstly, coating or growing active materials on metal wires has been proved effective for preparing FSSC electrodes. For instance, various carbon materials (e.g. electrochemically reduced graphene oxide and activated carbon) have been coated on gold, stainless steel wires to construct high performance FSSCs [11,12]. Meanwhile, transition metal oxides (e.g. MnO_2) and conducting polymers (e.g. polyaniline) have also been deposited on various metal wires for FSSC electrode applications [13–16]. However, owing to the intrinsically rigid feature of metal wires, the established FSSCs are still too tough for smart garments or other wearable electronics, which points out that achieving fully integratable energy storage devices remains a grand challenge for researchers. In addition, carbon fiber electrodes (e.g. carbon nanotube fibers [17,18], graphene fibers [19,20] and their hybrid fibers [21,22]) also exhibit compelling capacitive performance and versatility in FSSC applications. With various kinds of spinning technologies (e.g. dry spinning, wet spinning and coaxial spinning) been applied to this field, more and more carbon fiber based FSSCs with good mechanical property, well flexibility and elasticity have been developed. Nevertheless, the fabrication of these FSSCs generally involves complex preparation procedures and extremely rigorous conditions, which make them too costly to commercialization. So it is significantly meaningful to developed high-performance, low-cost FSSCs through low-cost and convenient fabrication procedures.

The core objective in designing smart garment is to endow it intelligent versatility while maintaining its comfortability. In this regard, fabricating functional fiber/yarn/thread by using existing textile is rather promising. Cotton thread (CT) is a macroscopic flexible and microscopic porous material composed of multiple individual weaving cotton fibrils, which again consists of multiple cotton microfibrils bundled together [23]. Due to its porosity, high knittability and inherent linear shape, CT is an ideal platform to fabricate electronic threads [24,25]. Furthermore, several FSSCs have been fabricated by modifying CT with activated carbon, carbon nanotubes and pen ink in the recent years [2,3,23,26].

Graphene is a one-atom-thick fabric of carbon uniquely combines supreme properties such as extreme mechanical strength, exceptional electronic and thermal conductivity, extraordinary elasticity and stiffness [27]. More importantly, graphene possesses the virtue of relatively low cost in comparison with carbon nanotubes, cause it is available for large-scale production from natural graphite through chemical methods [19]. Graphene fibers assembled by spinning technologies have already shown good performance in FSSCs [9,28,29], but considering their high prices and complicated preparation processes, exploring low cost and more convenient method to fabricate graphene-based FSSCs is still very urgent and attractive.

In this contribution, we reported an all-solid FSSC based on graphene hydrogels/multi-walled carbon nanotubes-cotton thread (GHs/MWCNTs-CT) fiber-shaped electrodes, which can be easily prepared from natural CT and graphene oxide/MWCNTs (GO/MWCNTs) mixture suspension via a hydrothermal process. In the hydrothermal process, GO sheets are hydrothermal reduced into GHs, and GHs/MWCNTs composites self-assemble onto the surfaces of the cotton fibers simultaneously. The obtained GHs/MWCNTs-CT is electrochemically active, highly flexible and mechanically robust. By coating GHs/MWCNTs-CT with polyvinyl alcohol-H_3PO_4 (PVA-H_3PO_4) gel electrolyte and twisting two strands of them together, we fabricated high performance FSSC. The FSSC is flexible and stable enough to be directly knitted into fabrics as well as maintaining its original capacitive performance.

2. Materials and experimental

2.1. Materials

Embroidery CT (DMC, France) with a diameter of approximately ~0.9 mm is comprised of 6 strands of intertwined filaments, which again consists of two hanks of cotton fibers twisted together. Graphite powder (HuaYi Group HuaYuan Chemical Industry Co. Ltd., China), MWCNTs (>95 wt%, Timesnano Co. Ltd., China), Bovine serum albumin (BSA) powder (Aladdin, USA), PVA (98–99% hydrolyzed, medium molecular weight, Alfa Aesar, USA) and other chemical reagents were used without further purification.

2.2. Experimental details

2.2.1. Preparation of GO

Graphite oxide was synthesized from graphite powder through a modified Hummers method [30,31]. GO suspension was prepared by sonicating graphite oxide dispersion for 2 h.

2.2.2. Preparation of purified MWCNTs

200 mg MWCNTs was added into mixed acid consisting of 30 mL H_2SO_4 (98 wt%) and 10 mL HNO_3 (65 wt%) to sonicate for 5 h. Then, 80 mL deionized water was added, after washed with abundant of deionized water, the product was dried at 60 °C for 24 h in vacuum. GO/MWCNTs mixture suspension (GO ~0.5 mg mL^{-1}, MWCNTs ~0.1 mg mL^{-1}) was prepared by sonicating GO/MWCNTs hybrids in deionized water for 30 min.

2.2.3. Preparation of BSA-functionalized CT

BSA solution (0.5 wt%) was prepared according to a reported literature [25]. For BSA functionalization, a piece of 10 cm long CT was dipped into BSA solution for 10 min at room temperature, then dried in fume hood.

2.2.4. Preparation of GHs/MWCNTs-CT

A 10 cm long BSA-functionalized CT and 20 mL GO/MWCNTs homogeneous suspension (pH: 3–4) were sealed in a 25 mL Teflon-lined autoclave and maintained at 180 °C for 30 min. After the autoclave naturally cooled to room temperature, the prepared GHs/MWCNTs-CT was taken out with tweezer and swilled with deionized water to remove any residues. Finally, the GHs/MWCNTs-CT was immersed in 1 M H_3PO_4 aqueous solution overnight and dried for fabricating FSSC.