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High-performance wearable supercapacitors fabricated with surface activated continuous filament graphite fibers

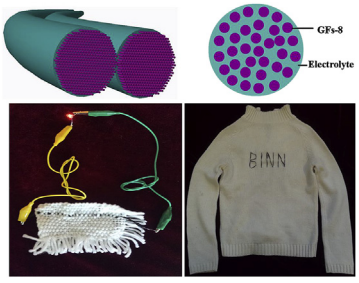
Dedong Jia [a], Xin Yu [a], Tinghan Chen [b], Shu Wang [a], Hua Tan [c], Hong Liu [c, *], Zhong Lin Wang [a, d, **], Linlin Li [a, ***]

[a] Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, National Center Nanoscience and Technology (NCNST), Beijing, 100083, PR China
[b] G1506, The High School Attached to Tsinghua University, Beijing, 100083, PR China
[c] State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, PR China
[d] School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, United States

HIGHLIGHTS

- Activated graphite fibers were synthesized after a rapid electrochemical oxidation.
- The activated sample exhibits much higher capacitance compared to pristine sample.
- A fiber supercapacitor based on activated graphite fibers was assembled.
- The fiber supercapacitor delivers high energy density and power density.
- The fiber supercapacitor with excellent flexibility could be easily weaved into cloth.

GRAPHICAL ABSTRACT



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ABSTRACT

Generally, carbon or graphite fibers (GFs) are used as the supporting materials for the preparation of flexible supercapacitors (SCs) by assembling various electrochemically active nanomaterials on them. A facile and rapid electrochemical oxidation method with a voltage of 3 V in a mixed H_2SO_4-HNO_3 solution for 2–15 min is proposed to active continuous filament GFs. Detailed structural characterization, SEM, TEM, XRD, Raman and XPS demonstrate that the GFs-8 (oxidized for 8 min) possessing high specific surface area which provided numerous electrochemical sites and a large number of oxygen-containing functional groups producing pseudocapacitance. Cyclic voltammetric (CV), galvanostatic charge-discharge measurements and electrochemical impedance spectroscopy (EIS) are conducted to test the capacitive of GFs and activated GFs. The capacitance of GFs-8 reaches as high as 570 mF cm^{-1} at the current density of 1 mA cm^{-1} in LiCl electrolyte, a 1965-fold enhancement with respect to the pristine GFs (0.29 mF cm^{-1}). The fabricated fiber solid-state supercapacitors (SSCs) provide high energy density of 0.68 mWh cm^{-3} at the power density 3.3 W cm^{-3} and have excellent durability with 90% capacitance retention after 10000 cycles. In addition, such fiber SSCs features flexibility and mechanical stability, which may have wide applications in wearable electronic devices.

* Corresponding author.
** Corresponding author. Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, National Center Nanoscience and Technology (NCNST), Beijing, 100083, PR China.
*** Corresponding author.
E-mail addresses: hongliu@sdu.edu.cn (H. Liu), zlwang@binn.cas.cn (Z.L. Wang), lilinlin@binn.cas.cn (L. Li).

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1. Introduction

Supercapacitors (SCs), also known as electrochemical capacitor, have attracted many interests due to their fantastic properties of ultrahigh output power density, fast charge/discharge capability and excellent cycling stability [1,2]. As an important class of energy storage device, SCs could be applied in electric vehicles and hybrid electric vehicles, back-up power systems and industrial energy management systems [3]. Most studies have primarily focused on liquid based SCs using aqueous solution, organic solution or ionic liquid as electrolytes [4–9]. However, the applications of SCs based on aqueous solution are hindered by two significant disadvantages. One is that the fabrication of these SCs demands high-cost packaging materials and technique to avoid the leakage of electrolytes, as the electrolytes are usually toxic and corrosive. The other drawback is that it is difficult to fabricate small and flexible SCs devices using liquid electrolytes, which have great demand in flexible electronics, and wearable electronic devices. Therefore, it is necessary to develop flexible solid-state supercapacitors (SSCs) devices with lightweight, excellent flexibility and high safety. This kind SSCs could be used as energy devices for portable electronic device, such as mobile phones, wearable electronics and portable flexible displays [10,11].

In order to fabricate high-performance flexible SCs, the physical flexibility, mechanical strength and electrochemical properties of the electrode must be taken into account. The carbon cloth and carbon paper that possess high mechanical strength, highly conductive, excellent bending property and good stability under ambient conditions have been extensively used as conductive substrates to fabricate flexible electrode. A variety of carbon clothes or carbon papers-based composite electrodes, such as Co_3O_4 [12], $Co_{0.85}Se$ [13], $CoSe_2$ [14], nanowire coated on carbon fiber paper, WO_3-X@Au@MnO_2 core-shell nanowires on carbon fabric [15], Zn_2SnO_4/MnO_2 core/shell nanocable-carbon fibers [16], $NiCo_2S_4$ [17] or $Ni(OH)_2$@$NiCo_2O_4$ [18] grown on carbon fiber paper, have been fabricated and exhibited attractive electrochemical performance. In addition, Lu et al. reported activated carbon cloth and carbon fiber paper by electrochemical oxidation and found the areal capacitances were enhanced after treatment [19,20]. However, those flexible SCs based on carbon clothes or carbon papers could only be attached to wearable cloth afterwards, but not be directly used as threads or fabrics woven to form wearable cloths [21]. With the widespread usage of wearable electronics, wearable SCs, especially fiber-shaped wearable SCs which are lightweight, flexible, and knittable have attracted increased attention in recent years [22–28]. For instance, the fibers SSCs were prepared using polymeric Kevlar fiber covered with ZnO nanorods [22], carbon microfiber bundles coated with multiwalled carbon nanotubes as a core electrode and carbon nanofiber paper as an outer electrode [23], and carbon fibers@pen ink [24]. However, the preparation process of those fiber SSCs was rather complex. Thus far, a few attentions has been paid to directly use pristine GFs for high-performance flexible SCs restricted by their low surface area and poor porosity [29–32]. Recently, Yu et al. reported a strategy to introduce high mesoporosity on carbon fibers by exfoliation annealing and reduction. Without adding electrochemical active material on them, the activated fibers showed a 22-fold increase up to 14.2 F cm^{-3} under 1000 mV s^{-1} [29]. Wang et al. found the carbon cloth via chemical oxidation followed by a two-step reduction process in hydrazine and ammonia exhibited a remarkable areal capacitance of 15.3 mF cm^2 at 1000 mV s^{-1} [30]. Zhou et al. reported a process for the preparation of porous core-shell carbon fibers by oxidation treatment and found those activated fibers had excellent electrical conductivity and mechanical [31]. In our previous work, GFs were oxidized through modified Hummers method, and used to fabricate scaly GO/graphite fiber electrodes for DNA biosensor [33]. However, those methods always need long treatment time and are complicated and high-cost, which is difficult to be scaled-up for industrial manufacture. Therefore, exploring facile and rapid method to fabricate fiber SSCs is still urgent and attractive.

Herein, we proposed a facile one-step electrochemical oxidation strategy to activate GFs and proved their implementation as high-performance electrode for flexible fiber SSCs. After electrochemical oxidation with a voltage of 3 V in a mixed H_2SO_4-HNO_3 solution for 8 min, a large number of functional groups were introduced onto the GFs-8 surface and the specific surface area simultaneously increased; whereas GFs-8 still maintained the excellent mechanical flexibility. The GFs-8 electrode delivered significantly improved capacitive performance compared with pristine GFs. For example, in the three-electrode text, the capacitance of GFs-8 was 570 mF cm^{-1} at 1 mA cm^{-1}, which was 1965 times higher than the untreated GFs (0.29 mF cm^{-1}). The GFs-8 can be used to assemble high-performance SSCs with excellent flexibility and wearability by using LiCl/PVA as the electrolyte. Particularly, the obtained fiber SSCs showed a remarkable energy density of 0.68 mWh cm^{-3} at the power density of 3.3 Wh cm^{-3} and 0.14 mWh cm^{-3} at the power density of 27.4 Wh cm^{-3}. As the threads, the flexible fiber SSCs could be weaved into clothe and light up a 3 V light-emitting diode (LED) indicator.

2. Experimental details

2.1. Materials

All reagents were of analytical grade and used without further purification. Sulfuric acid (95–98 wt% H_2SO_4) and nitric acid (65–68 wt% HNO_3) were purchased from Beijing Chemical Works. Polyvinyl alcohol (PVA) with degree of polymerization 1750 ± 50 was purchased from Tianjin Guangfu Fine Chemical Research Institute. $LiCl \cdot H_2O$ was purchased from Sinopharm Chemical Reagent Co., Ltd. The continuous filament GFs (M40-JB-12K) were obtained from Toray (Japan).

2.2. Synthesis of electrochemically activated GFs

Before activation, the GFs tows were cut into 6 cm in length and then cleaned by acetone, alcohol and deionized water in turn. The electrochemical activation was carried out in a conventional three-electrode cell with a mixture of concentrated H_2SO_4 and HNO_3 (V: V = 1: 2) for different time intervals. The washed GFs tow using as the working electrode was immersed into the solution for a depth of 2 cm. The reference electrode and counter electrode were a saturated calomel (SCE) electrode and platinum foil (2 cm × 2 cm), respectively. Then, the electrochemical activation was performed under a constant voltage of 3 V for required time. After the electrochemical oxidation process, the activated sample was taken out from the solution, washed with deionized water for several times, and dried for 3 h at 60 °C. Depending on the different activation time, the as-prepared samples were denoted as GFs-2 (activated for 2 min), GFs-5 (activated for 5 min), GFs-8 (activated for 8 min), GFs-10 (activated for 10 min) and GFs-15 (activated for 15 min), respectively.

2.3. Characterization

The morphology of the as-prepared samples was studied by a field emission microscope (FESEM) (HITACHI S-8020, Japan) at 5 kV. High-resolution transmission electron microscopy (HRTEM) images were obtained by a FEI/Tecnai G2F20 S-Twin TMP instrument