Journal of Power Sources 319 (2016) 271–280

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Conductive, tough, hydrophilic poly(vinyl alcohol)/graphene hybrid fibers for wearable supercapacitors

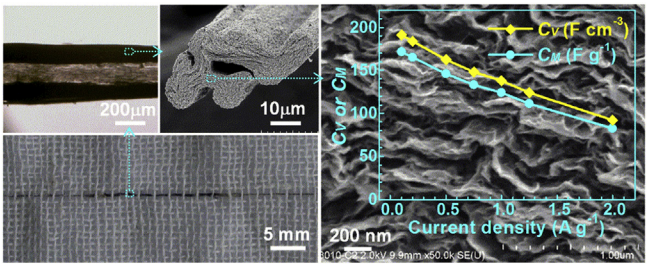
Shaohua Chen, Wujun Ma, Hengxue Xiang, Yanhua Cheng, Shengyuan Yang, Wei Weng, Meifang Zhu*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, PR China

HIGHLIGHTS

- Homogeneous mobile PVA/GO dispersions without gelation were successfully obtained.
- Continuous PVA/RGO hybrid fibers were produced by spinning and chemical reduction.
- The hybrid fibers shows obviously higher toughness, hydrophilicity and capacitance.
- A yarn supercapacitor was assembled and exhibits an energy density of 5.97 mW h cm^{-3}.
- The supercapacitor is flexible and robust enough to be weaved into a textile.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 November 2015
Received in revised form
4 April 2016
Accepted 6 April 2016
Available online 22 April 2016

Keywords:
Graphene hybrid fibers
Poly(vinyl alcohol)
Liquid-crystals
Wet-spinning
Wearable supercapacitors

ABSTRACT

Graphene fibers based flexible supercapacitors have great potential as wearable power sources for textile electronics. However, their electrochemical performance is limited by the serious stacking of graphene sheets and their hydrophobicity in aqueous electrolytes. Meanwhile, their brittleness is unfavorable for practical application. Incorporation of nanofillers into graphene fibers has been proved effective for enhancing their capacitance, whereas often leading to deteriorated mechanical strength. Herein we demonstrate that the strength, toughness and capacitive performance of graphene-based fibers can be significantly enhanced simultaneously, simply by incorporating hydrophilic poly(vinyl alcohol) (PVA) into a non-liquid-crystalline graphene oxide (GO) dispersion before wet spinning and chemical reduction. The structure and properties of the resulted PVA/graphene hybrid fibers are systematically investigated, and the mechanism behind these enhancements is discussed in detail. The hybrid fiber with a PVA/GO weight ratio of 10/90 possesses a strength of 186 MPa, a toughness of 11.3 J cm^{-3}, and a capacitance of 241 F cm^{-3} in 1 M H_2SO_4. A solid-state yarn supercapacitor assembled from these fibers exhibits a device energy of 5.97 mW h cm^{-3}, and features excellent flexibility and bending stability. This device is robust enough to be integrated into textile and thus promising as wearable power supply for smart textiles.

* Corresponding author.
E-mail address: zhumf@dhu.edu.cn (M. Zhu).

http://dx.doi.org/10.1016/j.jpowsour.2016.04.030
0378-7753/

1. Introduction

Smart textiles can integrate a lot of functional electronic components such as sensors, heating/illuminating elements, wireless modules, and actuators. Hence they will find various applications in the fields of health/sports/environmental monitoring [1], professional and military activities [2,3], and entertainment and fashion [4]. However, one major challenge for smart textiles is the development of wearable power supply that is flexible, robust and durable. Fiber-based supercapacitors (FSCs) have been considered as ideal candidates for this end, due to their flexibility and readily compatibility with textile processing [5]. In the last decade, a variety of intrinsic and modified fibers have been explored for this purpose, including carbon fibers [6–8], carbon nanotube (CNT) fibers [5,9,10], and graphene fibers [11–17]. Recently, great progress has been made in terms of energy density and power density [15,18]. Although showing lower mechanical strength and electrical conductivity than carbon fibers and CNT fibers, graphene fibers exhibit significantly higher specific capacitance due to graphene's ultrahigh specific surface area. Meanwhile, the cost of graphene fibers would be much lower, considering the abundance of its raw material-natural graphite, and the scalability of its production method-wet spinning from graphene oxide (GO) dispersion followed by reduction [19–21]. Therefore, graphene-based fibers have a greater potential in wearable energy storage.

Unfortunately, the specific capacitance of graphene fibers in aqueous electrolyte is far from the theoretical value of a single graphene sheet [12,13], due to the π–π stacking and hydrophobicity of graphene sheets. Two main strategies for the capacitance enhancement of graphene-based electrodes are to create a porous structure [22–25] and to improve the affinity to the electrolyte [26–29], which can also apply to graphene-based fibers. In our previous work, we demonstrated that both the porous structure and the wettability of graphene fibers play important roles on the electrochemical performance [20]. The benefit of a porous structure has been proved by the dramatically improved capacitive performance of an all-graphene fiber with porous sheath [12,30] and a highly porous neat graphene fiber [11]. Hybrid porous graphene fibers also show significantly enhanced capacitance, because of the spacer effect of various nanofillers such as MoS_2 and CNT [15,31–33]. However, the mechanical strength of both neat and hybrid porous graphene fibers are obviously deteriorated due to the presence of plenty of pores. Therefore, it is a great challenge to simultaneously enhance the mechanical and electrochemical property to meet the requirements of smart textiles.

It has been reported that the strength and toughness of CNT fibers can be enhanced by infiltration polymers into the fibers during or after the spinning process, such as poly(methyl methacrylate) [34], polyethylene [35] and poly(vinyl alcohol) (PVA) [36,37]. Low cost PVA is highly hydrophilic and compatible with GO, and could inhibit the stacking of GO sheets and hence reduced GO (RGO) sheets. Thus the mechanical and capacitive performances of RGO fibers would probably be improved by hybridizing RGO with appropriate amount of PVA. Gao's group has successfully assembled PVA-coated chemically-reduced graphene (CRG@PVA) hydrogel into nacre-mimicking CRG@PVA fibers with enhanced strength [38]. However, the preparation of CRG@PVA building blocks is time-consuming, and the low content of CRG (<50 wt%) in the fiber is not favorable for supercapacitor applications. In this work, conductive, tough and hydrophilic PVA/RGO hybrid fibers with high content of RGO were easily obtained by fast mixing of PVA solution with non-liquid-crystalline GO dispersion followed by continuous wet-spinning and chemical reduction. Results show that their mechanical strength, toughness, hydrophilicity and electrochemical performance are simultaneously enhanced at a significant degree compared with the neat RGO fibers. A solid-state yarn supercapacitor assembled from these hybrid fibers exhibits superior volumetric energy densities to the devices assembled from other reported graphene-based fibers. Meanwhile, this device is flexible and robust enough to be integrated into a textile, demonstrating its potential in wearable energy storage for smart textiles.

2. Experimental methods

2.1. Preparation of the RGO and PVA/RGO fibers

Graphite oxide (GtO) was prepared from flake graphite (1000 mesh, Shanghai Yifan Graphite) by Hummers' method [39] according to our previous report [20]. 2 g GtO was added into 98 g deionized water and exfoliated with a digital ultrasonic processor (S-450D, Branson) for 1 h. The resulting 2 wt% graphene oxide (GO) dispersion was liquid-crystalline (as confirmed by polarized optical microscope) with pH ≈ 2, and was denoted as pristine GO (PGO) dispersion. The basified GO (BGO) dispersion was obtained by addition of 10 M NaOH solution dropwise into 80 g PGO dispersion under stirring until the pH was around 11. After a further sonication for 5 min, the BGO dispersion was non-liquid-crystalline and flowed very easily [20]. A 2 wt% PVA solution was obtained by dissolving 1 g PVA (polymerization degree = 1700, saponification degree = 99%, Shanghai Petroleum) in 49 g deionized water at 95 °C for 1 h. Then it was mixed with the BGO dispersion at different PVA/GO weight ratios of 5/95, 10/90, 20/80 and 30/70 under sonication for 15 min. All the final PVA/BGO dispersions are homogeneous and easy-flowing, and are suitable for wet-spinning. In contrast, an immobile gel was formed when the PVA solution was blended with the PGO dispersion at a weight ratio of 30/70, and is not qualified for wet-spinning.

The RGO and PVA/RGO fibers were prepared by continuous wet-spinning followed by chemical reduction in the same way as our previous work [20]. The BGO and PVA/BGO dispersions were used as the spinning dope, respectively, and the jet stretch ratio was all controlled at 1.0. In a typical process, a PVA/BGO dispersion was loaded into a 10-ml syringe and injected into a rotating acetic acid bath through a 27 G needle at a speed of 1.5 m min^{-1}. The coagulated wet PVA/GO fiber was immediately drawn out of the bath, dried by a vertically-positioned infrared heater, and collected onto a winding pipe (Fig. 1g). Note that the simultaneous drying process guarantees that the GO and PVA/GO fibers adhere neither to themselves nor to the pipe. All GO and PVA/GO fibers were reduced in an aqueous HI solution (45%, Sinopharm) at 95 °C for 8 h [40], then washed alternatively by water and acetic acid for three times, and finally dried at 60 °C for 12 h in vacuum. The PVA/GO and PVA/RGO fibers are respectively named as P_xG_y and RP_xG_y fibers, where x and y are the percent weight ratio of PVA and GO in the dispersion for wet-spinning, respectively.

2.2. Assembly of a PVA/RGO yarn supercapacitor

A yarn supercapacitor was assembled from two bundles of PVA/RGO fibers as the working electrodes and a poly(ethylene terephthalate) (PET) yarn as the supporting substrate. Two bundles of five $RP_{10}G_{90}$ fibers (length = 1.7 cm) were arranged in parallel on a polypropylene sheet such that the length of the middle overlapped part is 1.5 cm. The PET yarn (length = 15 cm) was straightened, inserted closely between the two bundles, and fastened on the polypropylene sheet. The overhang ends (~0.1 cm) of the two bundles were adhered to the PET yarn by silver paste. Then the middle overlapped part (length = 1.5 cm) was carefully coated with $PVA/H_2SO_4/H_2O$ (1/1/10 in weight) gel electrolyte, so that a gap of