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High-performance yarn electrode materials enhanced by surface modifications of cotton fibers with graphene sheets and polyaniline nanowire arrays for all-solid-state supercapacitors

Chun Jin, Hai-Tao Wang, Ya-Nan Liu, Xiao-Hui Kang, Ping Liu, Jia-Nan Zhang, Li-Na Jin, Shao-Wei Bian*, Quan Zhu

College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, PR China

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ABSTRACT

A high-performance yarn electrode material, cotton/graphene/polyaniline, is synthesized by coating primary fiber cores inside cotton yarns with graphene sheets and followed by further growing polyaniline nanowire array layers through *in situ* polymerization of aniline. The electron transportation is enhanced by the 3D graphene conductive network on cotton fibers, which further bridges the polyaniline nanowires. The polyaniline nanowires with small diameters ensure high electrochemically active surface area. The spaces within the polyaniline nanowire array layers and the hierarchical pores of the entire yarn electrode benefit the fast electrolyte ion diffusion. The unique 3D yarn electrode structure results in an excellent electrochemical performance. The maximum areal capacitance and capacitance retention are 246 mF/cm^2 at 5 mV/s and 98% after 3800 cycles, respectively. A symmetric all-solid-state yarn supercapacitor is fabricated by using this yarn electrode, which delivers an energy density of 9.7 μWh/cm^2 at a power density of 840.9 μW/cm^2.

1. Introduction

The rapid development of wearable electronics is influencing our daily life in various ways, such as electronic textiles and implantable medical devices [1,2]. Powering these novel electronics needs high-performance energy storage devices with some key characteristics, such as flexibility, light weight, small volume and high electrochemical performance. However the conventional energy storage devices, such as batteries and capacitors, are unable to fully meet the requirement of wearable electronics because they are heavy, large and undeformed [3–7]. Among various flexible energy storage devices, flexible supercapacitors have aroused intensive attention in recent years due to their excellent properties, including lightweight, safe and flexible. They show huge potential in the wearable electronics [8–10].

The low electrochemical performance is one of the main issues which block the advancement of flexible supercapacitors. Lots of reported work indicated that the electrode materials directly determine the electrochemical performance. Hence, developing high-performance flexible electrode materials is a great challenge for excellent flexible supercapacitors. Nowadays, two-dimensional (2D) flexible thin-film electrode materials based on carbon cloth, graphene paper and carbon nanotube film have been proposed by using the top-down approach [11–15]. However, the small thickness of thin-film electrode materials not only blocks the improvement of energy storage performance, but also results in a fragile structure [16,17]. More importantly, they are hard to be incorporated in the daily clothing to power wearable electronics.

Compared to 2D thin-film electrode materials, one-dimensional (1D) yarn electrode materials, also called fiber electrode materials, have the potential to be woven or knitted into various desirable energy storage textiles, realizing the integration of flexible supercapacitors and daily clothing [17,18]. Meanwhile, they can also maximize the capacitance density due to their small volume. Recently, several 1D yarn electrode materials have been reported by using reduced graphene oxide fibers and carbon nanotube fibers [18,19]. Unfortunately, the compact electrode structure brought these pure carbon yarns with low electrolyte ion diffusion and ineffective surface area. The carbon nanotube composite yarn showed a low specific capacitance of 5 F/g [20]. These issues

* Corresponding author.
E-mail address: swbian@dhu.edu.cn (S.-W. Bian).

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severely limit their electrochemical performance and practical application. Metal yarns, such as gold, platinum, stainless steel and nickel, have also been used to fabricate 1D yarn electrode materials in recent years [21–23]. Miao et al., electrodeposited MO_2 on carbon nanotube/stainless steel composite yarns to form a electrode, which exhibited a volumetric capacitance of 217.61 F/cm^3 [22]. Shi et al., coated Au fibers with graphene sheets to form a graphene/Au yarn electrode. It exhibited a length capacitance of 11.4 μF/cm (0.726 mF/cm^2) [23]. Due to the absence of a porous structure, high mass density and/or volume fraction of metal fibers than those electrochemically active materials in metal yarn based electrodes, it is hard to achieve a satisfied gravimetric capacitance. Therefore, fabricating lightweight, flexible and high-performance porous yarn electrode materials by using cost-effective materials and a scalable fabrication process is still a great challenge.

The porous textile yarns constructed by many individual fibers are highly flexible, lightweight, low cost and mechanically robust, which can be easily weaved and knitted into daily clothing. These unique properties endow them with great potential in the fabrication of yarn electrode materials. However, textile yarns are unable to be directly applied in flexible electrode materials because they are electrically insulated and low electrochemically active in general. In order to achieve high electrochemical performance, the textile yarn electrode structure should be rationally designed to possess some properties including fast electron transportation, facile electrolyte ion diffusion and large active surface area. Functionalizing the fiber surface inside textile yarns with nanostructured active materials including carbon materials and pseudocapacitance materials is one of the most effective strategies for the enhancement of electrochemical performance.

Herein, a cotton/graphene/polyaniline (CT/G/PANI) composite yarn electrode material was designed and synthesized by modifying the primary cotton fiber cores with graphene sheet shells inside the CT yarn and followed by growing PANI nanowire array layers through *in situ* polymerization of aniline. The 3D hierarchically porous structure constructed by the cotton/graphen (CT/G) yarn and PANI nanowires ensures the rapid electrolyte ion diffusion and high active surface area of PANI for the Faradic redox reaction. Bridging the PANI nanowires with cotton/graphene conductive network further improves the electron transportation. The unique yarn electrode constructed by CT yarns, graphene sheet shells and PANI nanowire array layers creates a synergetic effect, which significantly enhances the electrochemical performance. The maximum areal capacitance and capacitance retention of CT/G/PANI yarn electrode material reached 246 mF/cm^2 at 5 mV/s and 98% after 3800 cycles, respectively. An all-solid-state symmetric supercapacitor device with a two-ply yarn structure was assembled by two identical CT/G/PANI yarn electrodes, which achieved a high energy density of 9.7 μWh/cm^2 at a power density of 840.9 μW/cm^2. It is believed that this textile yarn electrode material has great potential in flexible energy storage devices.

2. Experimental section

2.1. Synthesis of CT/GO and CT/G composite yarns

A commercial CT yarn was first cleaned by immersing it in 0.5 mol/L NaOH solution at 120 °C for 1 h. Then the CT yarn was washed with deionized (DI) water 3 times and dried at 50 °C in a vacuum oven.

Graphene oxide (GO) sheets were prepared according to a modified Hummer's method [24]. A cleaned CT yarn was immersed in 80 ml of 2 mg/ml GO suspension solution under stirring for 0.5 h. The CT/GO composite yarn was collected and dried at 50 °C for 2 h in a vacuum oven. The "immersing-drying" process was repeated several times to increase the GO loading mass. In order to convert GO to graphene, the CT/GO composite yarn was immersed in 0.1 mol/L $NaBH_4$ solution under stirring for 10 h. The resultant CT/G composite yarn was collected, washed with DI water and dried at 50 °C in a vacuum oven.

2.2. Synthesis of CT/G/PANI composite yarn electrode materials

A CT/G composite yarn was immersed in 40 ml of 1 mol/L H_2SO_4 solution containing 6.30×10^{-3} mol of aniline in an ice bath under stirring. After 20 min, 40 ml of 1 mol/L H_2SO_4 containing 28.5 mg of ammonium persulfate was carefully added into the above solution [25]. After 24 h, the CT/G/PANI composite yarn was collected, washed with DI water and dried at 50 °C in a vacuum oven.

2.3. Fabrication of all solid-state symmetric supercapacitor devices

3 g of PVA was first added in 30 ml of DI water. Then the solution was heated to 85 °C under stirring until it became clear. 3 g of H_3PO_4 was then added in the PVA solution under stirring after it cooled to the room temperature. Two CT/G/PANI composite yarns were immersed in the PVA/H_3PO_4 solution for 5 min and then dried at room temperature. Two identical CT/G/PANI composite yarns were twisted together and then coated with the electrolyte. The assembled yarn supercapacitor device with a two-ply yarn structure was dried at room temperature. Finally, the sealing film was used to wrap and seal the device.

2.4. Characterization

Scanning electron microscopy (SEM, Hitachi S-4800) was used to characterize the material structure and morphology. Raman spectroscopy was conducted by a Lab RAMHR 800 Raman

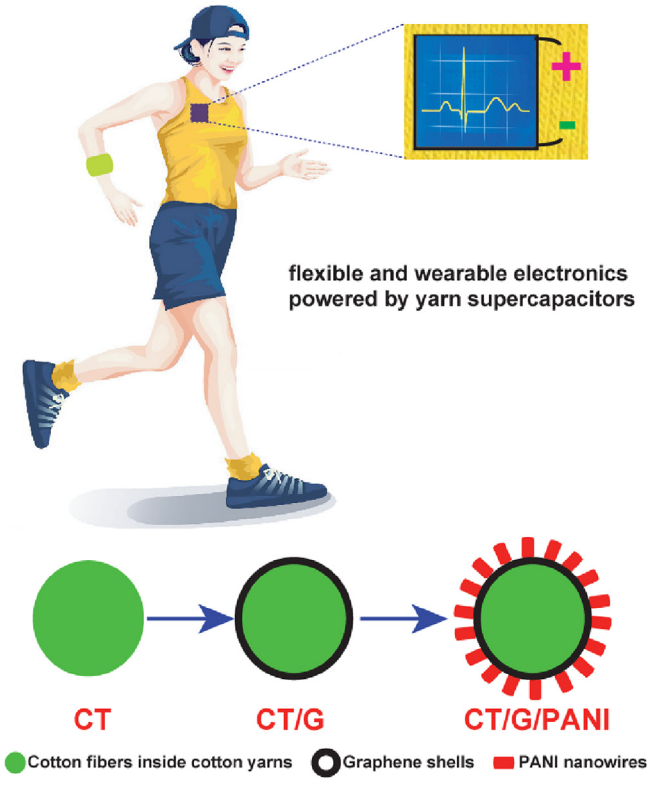

Fig. 1. Schematic illustration of the formation of flexible CT/G/PANI yarn electrode.