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Enhanced electrochemical properties of hierarchically sheath-core aligned carbon nanofibers coated carbon fiber yarn electrode-based supercapacitor via polyaniline nanowire array modification

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HIGHLIGHTS

- We report the scalable fabrication of sheath-core carbon fiber yarn-based electrode.
- The aligned carbon nanofibers were continuously coated on carbon fiber yarn.
- We enhance its electrochemical performance via PANI nanowire array modification.

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ABSTRACT

Scalable manufacturing of yarn-based supercapacitors with high energy density is highly desired for powering wearable electronics and smart textiles. In this paper, we report a novel type of sheath-core polyaniline nanowire array grown on aligned carbon nanofibers/carbon fiber yarn electrode (CFY@CNFs@PANI NWA) based supercapacitors. The carbon fiber yarn can maintain the yarn electrode with high electrical conductivity and mechanical properties. The introduced PANI NWA can further enlarge the specific surface area of the electrode and introduce pseudo-capacitance. The assembled solid-state supercapacitors show high areal specific capacitance of 234 mF/cm^2 at a current density of 0.1 mA/cm^2, and corresponded energy density of 21.4 μW h/cm^2 at power density of 0.52 mW/cm^2 in EMIMBF$_4$/PVDF/DMF gel electrolyte. The supercapacitors also exhibit ultrahigh rate capability (68%) and excellent cycle stability (90% after 8000 cycles). We also demonstrated that a 20-cm long supercapacitor can be readily to power up 36 pieces of red LEDs with a logo of "DHU". The scalable strategy paves a way towards mass production of wearable energy storage devices for smart textiles.

1. Introduction

Yarn- or fiber-shaped supercapacitors (YSCs or FSCs) with high power density, fast rate of charge-discharge and long cycling lifetime are ideal energy storage devices for wearable electronics [1]. Notably, the crucial component of FSCs is their flexible fiber electrodes which should possess both high energy density and proper mechanical properties including stretching, twisting and bending [2].

Carbonaceous fibers (i.e. graphene, carbon nanotube and carbon fibers) are very promising for FSCs. Carbon fiber and graphene fiber based FSCs usually show low specific capacitance and thus low energy density due to the lower specific surface area (SSA). There are two main strategies for enhancing electrochemical performance, which includes maximizing the specific surface area (SSA) [3] and/or introducing pseudo-capacitance by incorporating pseudocapacitive materials (i.e. conducting polymers and transition metal oxides). High SSA can be obtained by adding active carbons [4], or carbonized metal-organic framework [5]. Some works have reported that the addition of

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transition metal oxides for expanded spacing between carbon nanotube or graphene layers does not only increase SSA but also introduce pseudocapacitance for higher electrochemical performance [6,7]. Another approach is to employ conducting polymers, such as PANI, PEDOT, PPy, whose theoretical capacitances are 2000 F/g [8], 480 F/g [9,10] and 210 F/g [9,11], respectively. Among them, the decoration of CNT yarn with highly conductive PANI is considered to be very promising architecture for high EC performance, due to the relatively high SSA of CNT yarn and high theoretical specific capacitance of PANI [12–14]. For instance, Wang et al. fabricated a thread-like supercapacitor based on CNT yarns coated with PANI nanowire arrays which showed a specific capacitance of 12 mF/cm^2 at current density of 1 mA/cm^2 [13]. A similar two-ply yarn supercapacitor based on PEDOT:PSS/CNT yarns presented a capacitance of 18.5 F/g at the current density of 0.1 A/g [15]. Furthermore, reduced graphene oxide/CNT composite fibers coated with PANI were used for supercapacitors and got improved performance in the capacitance of 193.1 F/cm^3 at 1 A/cm^3 [16]. Although graphene fiber and CNT yarn based supercapacitors offer remarkable electrochemical and mechanical properties, they are expensive and difficult to scale up [17].

On the contrary, carbon nanofiber yarns (CNYs) hold great promise for high-performance YSCs, owing to the low cost, high SSA [15,18] and scalable manufacturing [19–21]. CNYs with well aligned carbon nanofibers are expected to have high electrical conductivity and specific capacitance. Moreover, the further coating with nanostructured conducting polymers on carbon nanofibers may further enhance the electrochemical performance via extra pseudo-capacitance and enhanced SSA [22].

In this work, we report a scalable method to continuously fabricate core-sheath polyaniline nanowire array grown on aligned carbon nanofibers/carbon fiber yarn electrode (CFY @CNFs@ PANI NWA) based supercapacitors. Electrochemical results show high specific capacitance (234 mF/cm^2 at 0.1 mA/cm^2) and energy density (5.2 μW h/cm^2 in PVA/H_2SO_4 electrolyte, 21.4 μW h/cm^2 in organic electrolyte), good rate capability and stable cycling life.

2. Experimental

2.1. Preparation of carbon fiber yarns @ PAN nanofibers (CFY@PAN NFs)

The core-shell yarns of carbon fiber yarns coated with PAN nanofibers were fabricated by the electrospinning system reported previously [23]. The system (Fig. 1a) is assembled with two metal needles with face-to-face configuration, a neutral metal disc and a hollow metal rod [23]. The PAN nanofiber coated carbon fibers were fabricated as follows: 10 wt% PAN in N, N-dimethylformamide (DMF) slurry was injected into the two needles which were applied with positive and negative voltages, respectively. The core fiber, carbon fiber (T300B-1K-50B, TORAY), passed through the rotated metal disc with electrospun nanofibers from needles twisted on the surface of carbon fiber and the yarn was withdrawn at a speed of 2 m/min. The amount of PAN NFs loaded on the CFY is ~16 wt%. The electrospinning parameters are summarized in Table S1 (Supporting Information).

2.2. Preparation of carbon fiber yarn @carbon nanofibers (CFY@CNFs)

The carbonization of CFY@PAN NFs was performed in a quartz tube furnace (OTF-1200X-S). The oxidation was conducted by oxidizing CFY@PAN NFs at a heating rate of 2 °C/min and keeping at 280 °C for 2 h under air atmosphere. The oxidized fibers were subsequently carbonized at 800 °C for 2 h under N_2 protection at a heating rate of 2 °C/min.

2.3. Preparation of carbon fiber yarn @carbon nanofibers @PANI nanowire array (PANI NWA@CNFs@CFY)

The PANI nanowire arrays on CFY@CNFs were obtained with the in-situ polymerization of aniline in aqueous hydrochloride acid (HCl) solution. Typically, CFY@CNFs was immersed into 30 ml HCl solution (1 M) with the subsequent addition of a certain concentration (0.01 M, 0.02 M and 0.04 M) of aniline monomers. The oxidant solution was prepared by adding ammonia persulfate (APS, molar ratio between aniline and APS is 1:1) into 20 ml of 1 M HCl and cooling down to 0–4 °C in a freezer. The APS solution was then dropwise added into the aniline solution. The mixture was gently stirred for 6 h in an ice bath. The resultant CFY@CNFs@PANI NWA was washed with deionized water and ethanol repeatedly, and finally dried overnight at 60 °C in vacuum.

Fig. 1b shows the fabrication process of the CFY@CNFs@PANI NWA electrodes. The carbon fiber yarn works as a current collector deemed to enhance electrical and mechanical properties of CNFs. The subsequent in situ polymerization of aniline was conducted in aqueous hydrochloride acid solution to achieve the hierarchical core-sheath CFY@CNFs@PANI NWA electrodes (Fig. 1b).

2.4. Assembly of fiber shaped SCs

FSCs were fabricated with CFY@CNFs@PANI NWA as electrodes and current collectors. Firstly, PVA/H_2SO_4 gel electrolyte was formed as follows. 1 g polyvinyl alcohol (PVA, 80% hydrolyzed) was added into 10 ml DI water by stirring it at 80 °C for 1 h, after which 0.98 g H_2SO_4 was mixed with it. Secondly, to assemble all-solid-state FSSCs, two fiber-shaped electrodes were placed in parallel on a PET substrate and immersed in PVA/H_2SO_4 gel electrolyte. The end of each fiber electrode was fixed and connected with a copper foil by silver paint. The assembled FSSCs were placed at room temperature until they completely solidified.

2.5. Characterizations

Fourier transform infrared spectroscopy (FTIR) measurements were taken by (Spectrum Two, PerkinElmer). Scanning electron microscopy (SEM) images were obtained from TM 3000 and HITACHI SU4800.

The EC properties of these FSSCs were tested by an EC workstation (CHI 660E, CH Instruments Inc.). For these fiber-based SCs, cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and EC impedance spectra (EIS) (0.01 Hz - 100 kHz) were measured by a two-electrode method. The cycling behavior was performed with the CT 2001A battery program controlling test system (China-Land Co., Ltd). The diameter and length of the yarn immersed into the electrolyte were measured precisely by a microscope and vernier calipers. The equation $A = \pi DL$ was used to calculate the surface area of single electrode, where D and L are the diameter and length of yarn electrode, respectively. The specific capacitance, energy density and power density were calculated according to reference [24]. The specific capacitances (C_A) in two-electrode system was calculated from the cyclic voltammetry curves, using $C_A = \left(\int_{U_1}^{U_2} IdU + \int_{U_2}^{U_1} IdU \right) / (A \times u \times (U_2 - U_1))$, where A, u, U_1, U_2, and I are the surface area of single electrode, scanning rate, minimal and maximal potential of CV test, and the instant current of CV curves, separately. C_A can also be calculated by galvanostatic charge/discharge test, $C_A = (I \times t)/(\Delta U \times A)$, where I, t, ΔU, A are the discharge current, the discharge time, the potential window and surface area of single eletrode, separately. Here C_A is the specific capacitance of single fiber-shaped electrode. The whole fiber-based SC is $C_{tA} = \frac{1}{4} C_A$. The volume and linear specific capacitance of the single electrode are $C_V = C_A \times A/V$ and $C_L = C_A \times A/L$, separately, where A, V, L are surface area of single electrode, volume of single electrode, and length of single