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Core-shell structured carbon nanofibers yarn@polypyrrole@graphene for high performance all-solid-state fiber supercapacitors

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ABSTRACT

Carbon nanofibers yarns (CNY) have been prepared by carbonizing twisted electrospun PAN nanofibers, which can be used as the electrode of fiber-shaped all-solid-state supercapacitor after depositing conductive polymer of polypyrrole (PPy) and reduced graphene oxide (rGO) on their surface to form a core-shell structure (CNY@PPy@rGO). The flexible and binder-free fiber supercapacitors with PVA/H_3PO_4 gel electrolyte have a high specific capacitance (92.57 F/g, 80.46 F/cm^3, 836.87 mF/cm^2, and 111.46 mF/cm of C_M, C_V, C_A, and C_L, respectively, at the scan rate of 2 mV/s) thanks to the core-shell structure and synergistic effects of three conponents. It also shows high cycling performance with 86% capacitance retention after 10000 cycles with excellent flexibility and stability at different bending angles.

1. Introduction

Flexible, portable, and wearable electronic devices, such as smart clothes and foldable electronic displays have been developed in the past decades [1–5], which requires flexible and wearable energy storage devices with high specific capacitance. Supercapacitors have high power density, long cycling life, good stability, and faster charging and discharging rate compared to secondary batteries [6–9]. Recently, fiber-shaped all-solid-state supercapacitors with excellent stability and flexibility have drawn tremendous attentions as power source in some wearable applications by knitting or co-weaving them into other textiles.

In most fiber-shaped all-solid-state supercapacitors, carbon nanotubes (CNTs) and graphene fibers have been commonly used as flexible electrodes materials due to their excellent electrochemical properties [10–13]. Nevertheless, the high cost of CNTs or graphene fibers hinders their scalable applications of fiber-shaped supercapacitors [14,15]. Therefore, developing a facile and scalable route to prepare flexible and free-standing fiber electrodes with high electrochemical performances for fiber-shaped all-solid-state supercapacitors is still a great challenge.

Recently, carbon nanofibers derived from electrospun PAN nanofibers have attracted great attentions as a promising electrode of supercapacitors, owing to their high electrical conductivity, large specific surface area, and excellent mechanical property [16–20]. In our group, carbon nanofibers were used as a flexible substrate for deposition of conductivity polymer or red phosphorus for high performance supercapacitor and sodium ion battery, respectively [21,22]. In addition, PPy is a potential electrode material for fiber-shaped supercapacitor, due to its high specific capacitance performance, scalable and facile synthesis [23–25]. Furthermore, thin carbon layer coated on the surface of conductive polymer can both improve the specific capacitance and cycling stability [26–28].

In this work, we have developed a facile and scalable route to prepare flexible and binder-free carbon nanofibers

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yarn@polypyrrole@reduced graphene oxide (CNY@PPy@rGO) core-shell fiber electrode for high performance symmetric fiber-shaped all-solid-state supercapacitors. As shown in Fig. 1, CNY were fabricated by carbonizing the elelctrospun PAN nanofibers yarn, and used as the flexible substrate and electrical double layer capacitance material. PPy was deposited on the surface of carbon nanofibers by in-situ electrochemical deposition to improve the electrochemical performance, while decrease the cycling stability. Therefore, we design the reduced graphene oxide layer coating on the surface of CNY@PPy fiber to improve both the specific capacitance and cycling stability of fiber-shaped supercapacitor based on CNY@PPy@rGO fiber electrode.

2. Experimental section

2.1. Materials

The expandable graphite (2000 meshes) was from Henglide Graphite Company (Qingdao, China). Polyacrylonitrile (PAN, average $M_w = 150000$) powder was from Sigma-Aldrich Ltd., America. Pyrrole monomer, sodium perchlorate, and polyvinyl alcohol (PVA, $M_w = 145000$) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd, China. All other reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China without any further treatment.

2.2. Preparation of graphene oxide

Graphene oxide was prepared by the modified Hummers method [29] (as reported in our earlier work [30]) from expandable graphite with small size particle (2000 meshes) to ensure that GO sheets can be uniformly coated on the surface of CNY@PPy fiber.

2.3. Preparation of CNY, CNY@PPy, and CNY@PPy@rGO film

PAN nanofibers film was deposited on a piece of aluminium foil by an electrospinning process for 3 h using a precursor solution (2 g PAN powder in 18 g DMF). The applied voltage, distance between the tip of spinneret and the collector, and the flow rate is 18 KV, 15 cm, and 0.03 mL/min, respectively. A ground roller with aluminum foil was used as a collector at the rate of 400 rpm. PAN nanofibers film was peeled off from aluminium foil after 50 °C for 5 h to remove the residual solvent. PAN nanofibers yarn was prepared by spun from one side of PAN strip with size of 150 × 30 mm using electric motor with about 500 turns per meter (Fig. 1a). Finally, CNY was fabricated by stabilizing PAN nanofibers yarn at 280 °C for 5 h with the heating rate of 1 °C/min under air atmosphere, and then carbonizing at 1000 °C for 2 h with the heating rate of 5 °C/min under a flowing Ar atmosphere.

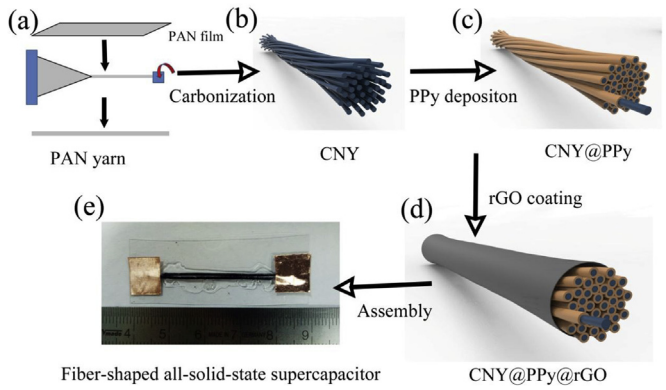

Fig. 1. Fabrication process of fiber materials and fiber-shaped all-solid-state supercapacitors (a) Schematic illustration of fabricating PAN nanofibers yarn. (b) Schematic structure of CNY fiber electrode. (c) Schematic structure of CNY@PPy fiber electrode. (d) Schematic structure of CNY@PPy@rGO core-shell fiber electrode. (e) The digital photograph of fiber-shaped all-solid-state supercapacitor. (A colour version of this figure can be viewed online.)

The as-prepared CNY fiber with length of 30 mm was firstly immersed into 0.3 M $NaClO_4$ aqueous solution containing 5% (v/v) pyrrole monomer for 30 min. Then, the CNY fiber was directly used as the working electrode of a three-electrode electrochemical workstation (CHI660E Instruments, Shanghai, China) under a potential of 0.8 V. The Pt electrode and Ag/AgCl were used as the counter and reference electrodes, respectively. CNY@PPy fibers with different PPy loadings were prepared by adjusting the electrochemical deposition time. CNY@PPy@GO core-shell fiber electrodes were prepared by directly immersing CNY@PPy fiber into GO solution (2 mg/mL) for 2 h and dried in air. Then, GO was reduced in 55% HI solution at 95 °C for 15 min. CNFs@PPy@rGO core-shell fibers were obtained after immersing in DI water to remove extra HI.

2.4. Characterization of the samples

The morphology and structure of all materials were characterized by field emission scanning electron microscope (SEM, Hitachi SU-70, Japan). The specific surface area of CNY was determined from the N_2 adsorption isotherm at 77 K by using the ASAP 2020 (Micromeritics, USA). Raman spectra were obtained on Renishaw InVia Reflex using 633 nm as the excitation laser.

2.5. Fabrication of flexible symmetric fiber-shaped all-solid-state supercapacitors

To assemble a symmetric fiber-shaped all-solid-state supercapacitor, two CNY@PPy@rGO core-shell fiber (length of the overlapped portion is 30 mm) were aligned in parallel on the PET substrate with size of 20 × 50 mm (Fig. 1e), soaked with PVA/H_3PO_4 gel electrolyte, and dried at room temperature. The PVA/H_3PO_4 gel electrolyte was prepared by mixing PVA (3 g) and H_3PO_4 (3 g) in 30 mL of deionized water and heated at 90 °C under stirring until the solution became clear.

2.6. Electrochemical performance measurements

All electrochemical measurements including cyclic voltammograms (CV), galvanostatic charge/discharge (GCD) curves of fiber-shaped all-solid-state supercapacitor were carried out using electrochemical workstation (CHI660E Instruments, Shanghai, China). Electrochemical impedance spectra (EIS) measurements were performed in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an AC perturbation of 10 mV.

The specific mass capacitance (C_M), volumetric capacitance (C_V), area capacitance (C_A), and length capacitance (C_L) of the symmetric fiber-shaped all-solid-state supercapacitors were calculated according to $C_M = 2C/M_{fiber}$, $C_V = 2C/V_{fiber}$, $C_A = 2C/S_{fiber}$, and $C_L = 2C/L_{fiber}$, respectively, where C can be calculated from the CV curves according to the following equation:

$$C = \left({}^{1}/_{2v}\right) \times \int IdV/\Delta V \quad (1)$$

where I is the response current (A), ΔV the potential window (V), v the scan rate (mV/s). M_{fiber}, V_{fiber}, S_{fiber} and L_{fiber} are the mass, volume, surface area, and length of the overlapped portion single fiber electrode, respectively. In this paper, $S_{fiber} = \pi \times D \times L$ is the surface area of a single fiber electrode, and $V_{fiber} = 2 \times \pi \times (D/$