



Three-dimensional non-woven poly(vinyl alcohol-co-ethylene) nanofiber based polyaniline flexible electrode for high performance supercapacitor



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ABSTRACT

Polyaniline (PANI) has been fabricated on three-dimensional polyethyleneterephthalate (PET) coated with poly(vinyl alcohol-co-ethylene) nanofibers (NFs) substrate through a facile in-situ chemical oxidative polymerization method. With various concentrations of NFs, a series of PANI/NFs/PET-*x* flexible electrodes have been successfully obtained. Among them, the PANI/NFs/PET-5.4 (NFs mass loading of 5.4 g m⁻²) electrode displays the highest conductivity of 0.75 S cm⁻¹, and the largest areal capacitance of 1.47 F cm⁻² (503 F g⁻¹) at 1 mV s⁻¹ or 1.58 F cm⁻² (543 F g⁻¹) at 1.0 mA cm⁻². Furthermore, symmetric supercapacitor is assembled, exhibiting high power density (20.11 W m⁻²), energy density (0.61 Wh m⁻²) and cycling stability. This can be ascribed to the NFs, which not only provides high conductivity for electron transport, but also mitigates the degradation of PANI through the synergistic effect between NFs and PANI.

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1. Introduction

With the rapid development of portable and wearable electronics, flexible energy storage has attracted tremendous research interests [1,2]. Among these devices, flexible supercapacitors, which endowed with the merits of high power density, long cyclic stability, and wearability, hold great promises recently [3–6]. Furthermore, compared with conventional rigid preparations of electrode for supercapacitors, flexible electrodes ease the fabrication procedure without the usage of binder, and the conductivity can be enhanced simultaneously [7,8]. Especially for the three-dimensional structures, they have attracted much interests due to their superior properties and potential application prospects [9–12]. As such, the key to realize their application relies on the fabrication of electrode materials.

Polyaniline (PANI) has been extensively studied as conducting polymer of pseudocapacitive electrode material due to its

remarkable theoretical capacitance, high conductivity in the doped state, fast redox protonation/deprotonation reactions, facile synthesis, low cost, and lightweight features [13,14]. However, the swelling, shrinkage, and irreversible degradation of PANI during the charge/discharge process lead to poor stability [14,15]. Besides, the conductivity of PANI in deprotonation state is low as well [16]. Cellulose fibers and carbon-based materials (graphene, carbon nanofibers, carbon nanotubes) are typical substrates commonly coupled with PANI, which is an effective approach to enhance the cycling stability of the flexible electrode. For instance, Liu et al. [5] deposited PANI onto the rGO/cellulose fibers composite paper by a “dipping and drying” strategy, which achieved a specific capacitance of 465 F g⁻¹. Additionally, cellulose-derived framework coated by PANI demonstrated areal capacitance of 3297.2 mF cm⁻² (220 F g⁻¹), and the network guaranteed more than 83% capacitance retention [17]. In particular, the polymer nanofibers, which provide intrinsic inter-fiber porosity and high specific surface area, are promising candidates as supporting materials for high electrochemical performance electrodes.

Poly(vinyl alcohol-co-ethylene), a hydrophilic thermoplastic copolymer of ethylene and vinyl alcohol, has wide applications in microbial fuel cell anode [18], catalytic hydrogenation [19], and

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pressure sensor [20]. Moreover, the abundant hydroxyl groups on poly(vinyl alcohol-co-ethylene) nanofibers (NFs) make it attractive as the polymer matrix [21]. The 3D porous network constructed by NFs substrates can offer much more contact area between electrolyte and electro-active material [22]. On the other hand, the functional groups can be utilized to deposit and stabilize the electro-active materials. Nevertheless, few attention has been paid to adopting poly(vinyl alcohol-co-ethylene) nanofibers as flexible substrate.

Herein, by spraying NFs onto three-dimensional intertwined non-woven fabric polyethyleneterephthalate (PET) as substrate, PANI/NFs/PET- x ($x = 4.0, 5.4, 7.1$) flexible electrodes have been synthesized through in-situ chemical oxidative polymerization approach. The surface morphology is made up of PET or NFs/PET substrate coated by PANI. Besides, one-dimensional PANI nanowires or its aggregations are interconnected with each other on the nanofibers. The influence of the NFs with various mass loadings on the conductivity and electrochemical properties are discussed in detail. With the optimized PANI/NFs/PET-5.4 as flexible electrode, areal capacitances of 1.47 F cm^{-2} or 503 F g^{-1} at 1 mV s^{-1} has been obtained, which are higher than PANI/PET electrode (1.22 F cm^{-2}), indicating the positive effect of NFs.

2. Experimental section

2.1. Preparation of poly(vinyl alcohol-co-ethylene) nanofibers (NFs)/PET- x

The NFs were prepared according to our previously published procedures [18,19]. Briefly, the mixture of CAB and poly(vinyl alcohol-co-ethylene) with a certain ratio was fed into a twin-screw extruder. Thus, CAB/poly(vinyl alcohol-co-ethylene) nanofibers were prepared through a melt spinning technique. Then, the NFs in form of continuous yarns were obtained by the extraction of CAB matrix using acetone as a solvent.

1 g NFs were dispersed in the mixed solvent of isopropanol and deionized water (volume ratio is 1:1, 100 mL). Subsequently, the homogenized solution was sprayed onto both sides of PET non-woven fabric ($5 \text{ cm} \times 5 \text{ cm}$) and then dried at ambient temperature. And the product was designated as NFs/PET. By changing the amounts of NFs, a series of NFs/PET- x ($x = 4.0, 5.4$ and 7.1 gm^{-2}) was obtained, keeping the other preparation conditions same.

2.2. Preparation of PANI/NFs/PET- x and PANI/PET

0.93 g aniline monomer was dissolved into 30 mL deionized water in a beaker, followed by the addition of 5 mL HCl solution. Flexible substrate NFs/PET- x was immersed into above suspension, and ultrasonicated for 1 h. After that, the beaker was placed in an ice bath environment, while the solution was kept stirring. Subsequently, 30 mL 0.33 M ammonium peroxydisulfate (APS) solution was added dropwise to above mixture. The resulting solution was further stirred for 24 h, accompanied with the color from blue to dark green. The as-obtained product was rinsed with deionized water and ethanol several times, and finally dried at room temperature to result in the flexible PANI/NFs/PET- x ($x = 4.0, 5.4$ and 7.1 gm^{-2}) electrode with thickness of 337, 353 and 379 μm , respectively. For comparison, PANI/PET (thickness: 297 μm) was prepared without the addition of NFs, keeping the other conditions fixed. The schematic illustration of the preparation procedures and electrochemical test configurations of PANI/NFs/PET- x and PANI/PET are depicted in Scheme 1.

2.3. Fabrication of all-solid-state symmetric devices

The $\text{H}_2\text{SO}_4/\text{PVA}$ gel electrolyte was prepared as follows. 1 g PVA powder and 0.8 g H_2SO_4 were added into 10 mL deionized water. Then the mixture was heated at 90°C under stirring. When the PVA powder was totally dissolved and the solution became clear, the solution was cooled down and the $\text{H}_2\text{SO}_4/\text{PVA}$ gel electrolyte was obtained. The PANI/NFs/PET-5.4 electrodes were dipped into the gel electrolyte. After permeation of the gel electrolyte into electrodes and the evaporation of excess water, all-solid-state symmetric device was assembled. The thickness of gel electrolyte between PANI/NFs/PET-5.4 was about 300 μm .

2.4. Materials characterization

The morphology and composition of the samples were taken by scanning electron microscopy (SEM, JEOL, IT-300) equipped with energy dispersive X-ray analysis system (EDS, JEOL). The functional groups were determined by Fourier transform infrared spectroscopy (FTIR, Bruker, Tensor 27). The conductivity of the products was analyzed using four-probe (RTS-9, Guangzhou 4 Probe Tech) method.

2.5. Electrochemical measurements

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on electrochemical workstation (Autolab PGSTAT302 N, Metrohm AG, Switzerland). Galvanostatic charge-discharge tests were carried out using a multichannel battery-testing device (LAND CT 2001A, Wuhan Landian Electronic). CV tests were conducted at scan rates of $1\text{--}100 \text{ mV s}^{-1}$. EIS were recorded in the frequency range of $100 \text{ kHz}\text{--}0.01 \text{ Hz}$ with the amplitude of 5 mV. Galvanostatic charge-discharge programs were set over the potential window from 0 to 0.8 V. A three-electrode system was used to investigate the capacitive behavior of single electrodes in 2.0 M NaCl/HCl aqueous solution ($\text{pH} = 1$). The flexible electrodes with sizes of $1.5 \text{ cm} \times 0.9 \text{ cm}$ served as working electrode, while platinum plate and KCl saturated calomel electrode (SCE) served as counter and reference electrode, respectively. Symmetric supercapacitor assembled by two identical working electrodes was tested in a two-electrode system. Besides, the all-solid-state symmetric devices were tested in a constant galvanostatic charge-discharge process at current density of 3 mA cm^{-2} .

The areal capacitances (C_{ac} , F cm^{-2}), discharging areal capacitance (C_d , F cm^{-2}), energy density (E_d , Wh m^{-2}) and power density (P_d , W m^{-2}) of the flexible materials in three-electrode and two-electrode cell configurations can be calculated on the basis of following equations:

$$C_{ac} = \left(\int IdV \right) / (vA\Delta V) \quad (1)$$

$$C_d = (I\Delta t) / (A\Delta V) \quad (2)$$

$$E_d = (C_d\Delta V^2) / (2 \times 0.36) \quad (3)$$

$$P_d = 3600 \times E_d / \Delta t \quad (4)$$

where $\int IdV$ is the integral area of the CV curve, v (mV s^{-1}) is the scan rate, ΔV (V) is the potential window, A (cm^2) is the area of the electrode, I (A) is the discharge current and Δt (s) is the discharge time. And the gravimetric specific capacitance were calculated

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