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Polypyrrole/reduced graphene oxide coated fabric electrodes for supercapacitor application

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ABSTRACT

Flexible and wearable energy storage devices are strongly demanded to power smart textiles. Herein, reduced graphene oxide (RGO) and polypyrrole (PPy) were deposited on cotton fabric *via* thermal reduction of GO and chemical polymerization of pyrrole to prepare textile-based electrodes for supercapacitor application. The obtained PPy–RGO-fabric retained good flexibility of textile and was highly conductive, with the conductivity of 1.2 S cm^{-1}. The PPy–RGO-fabric supercapacitor showed a specific capacitance of 336 F g^{-1} and an energy density of 21.1 Wh kg^{-1} at a current density of 0.6 mA cm^{-2}. The RGO sheets served as conductor and framework under the PPy layer, which could facilitate electron transfer between RGO and PPy and restrict the swelling and shrinking of PPy, thus resulting in improved electrochemical properties respect to the PPy-fabric device.

1. Introduction

Smart textiles (or E-textiles) are a novel type of fabrics that are capable of sensing, data processing, actuating, generating/storing power and/or communicating [1,2]. These textiles have gained strong interest in recent years due to their potential applications in embedded biomedical monitors, high-performance sportswear, wearable displays, military garment devices, and so on [3–7]. The widespread commercialization of smart textiles is restricted by the lack of integrated energy storage, since conventional batteries and supercapacitors are too bulky, rigid and heavy [8]. Therefore, it is very imperative to develop energy storage devices on textile structures that are generally used in the garment industry.

Cotton fabric, one of the most universal textiles, is made from natural cotton fibers, which possess a hierarchical structure with high porosity, large surface area and hydrophilic functional groups [9]. Each cotton fiber is constructed of multiple cellulose fibrils, which are in turn constituted by multiple microfibrils bundled together. This specific structure can improve the adhesion and distribution of active materials on the fabric. As a result, the cotton fabric has been widely used as a substrate for the development of wearable electrodes [9–16].

Carbonaceous materials such as graphene, carbon nanotubes (CNTs), and porous activated carbon have been combined onto cotton fabrics to fabricate textile electrodes for batteries and supercapacitors in recent years [5,9,11,17–19]. Hu et al. produced stretchable supercapacitors *via* coating single-walled CNTs on cotton fabrics, achieving a specific capacitance up to 140 F g^{-1} and a high specific energy [9]. Gogotsi's group reported carbon-coated fabric supercapacitors by screen-printing porous activated carbon onto cotton fabrics [18]. The devices exhibited a specific capacitance of 85 F g^{-1} as well as a capacitance decrease of 8% over 10,000 cycles. However, the main weakness of carbonaceous materials used in supercapacitors is generally considered to be their low specific capacitance.

Conducting polymers, including polypyrrole (PPy), polyaniline, polythiophene and their derivatives, are especially suitable for flexible electrodes due to their good conductivity, mechanical flexibility, high theoretical capacitance, and fast redox properties [20–22]. The ability to store charges in the case of conducting polymers results from a doping–dedoping process. Conducting polymers have also been proven to be useful in fabricating textile electrodes. Yue et al. developed a stretchable electrode by coating PPy onto a commonly available nylon lycra fabric, which even showed improved electrochemical properties when being stretched [23]. In our previous work, PPy-coated cotton fabric electrodes were prepared through *in situ* chemical polymerization using various templates, achieving specific capacitances of 225–304 F g^{-1} [14–16]. However, the practical application of textile electrodes based on conducting polymers is limited by their poor cycling stability.

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Graphene is considered to be very hopeful as energy storage material due to its unique properties of high specific surface area, superior electrical conductivity, favorable flexibility and good mechanical stiffness. Graphene has attracted much attention in the preparation of conducting polymer-based composites for supercapacitor applications [24–27]. However, there are few literatures reported about conducting polymer–graphene composites used to construct textile electrodes [28]. In this work, we prepared PPy/reduced graphene oxide (RGO)-coated cotton fabrics via thermal reduction of graphene oxide (GO) and consequent chemical polymerization of pyrrole. The electrochemical properties of the textile supercapacitor based on the PPy–RGO-fabric electrodes were investigated.

2. Experimental

2.1. Materials

Cotton fabric with a surface density of 114 g m^{-2} was supplied by Wuhan Rongsheng Printing and Dyeing Co., Ltd. All the chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd., and were used as received. Ultrapure water with a resistivity of near to 18 MΩ cm obtained from a Milli-Q Advantage system was used to prepared aqueous solutions.

2.2. Preparation of RGO-coated fabric

GO was prepared according to chemical oxidation of graphite flakes using a modified Hummers method [29,30], which was then ultrasonicated at room temperature for 30 min to form a stable suspension with a concentration of 2 mg ml^{-1}. The cotton fabric was cleaned with an aqueous solution of scouring and sodium carbonate for 1 h, rinsed with abundant water and then dried completely under vacuum for 24 h. The fabric piece (1×3 cm^2) was dipped into the GO suspension at room temperature under sonication for 30 min and rinsed with water and ethanol to remove unattached GO. After that, the GO-fabric was dried at 80 °C for 2 h. The RGO-coated fabric was obtained by annealing the GO-fabric at 250 °C under N_2 atmosphere for 2 h.

2.3. Preparation of PPy–RGO-coated fabric

PPy was deposited onto the RGO-fabric by chemical polymerization according to our previous reports [14–16]. Briefly, the RGO-fabric (1×3 cm^2) was immersed in a 50 ml aqueous solution of Py (1 M) and stirred for 30 min. Then, 50 ml aqueous solution of ferric chloride (0.5 M) was added dropwise into the reaction mixture. The polymerization was performed in an ice bath for 2 h under stirring. The fabric product was washed with 0.5 M hydrochloric acid and water, and vacuum-dried overnight at 50 °C. The control PPy-coated fabric was also prepared according to the same procedure using the raw fabric.

2.4. Characterization

The surface conductivity of the fabric electrodes was measured by an RTS-9 four-probe multimeter (Guangzhou 4Probes Tech Industrial Co., Ltd., China) using copper electrodes. The flexibility test was performed on a homemade probe table, on which a steady potential was applied from a constant power supply and the current across the probes was recorded using a digital multimeter. The surface morphology was probed with a scanning electron microscopy (SEM, JEOL JSM-6510LV, Japan) at different magnifications. The samples were attached onto the microscope stage with double-sided conductive carbon tape and then a thin gold layer (~3 nm) was sputter-coated to get good electrical contact. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected with a TGA-FTIR spectrometer (Bruker Tensor 27, Germany).

A symmetric supercapacitor device was assembled to test the electrochemical properties of the fabric electrodes with 2.0 M NaCl aqueous solution as electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out with an Autolab PGSTAT302N potentiostat/galvanostat analyzer (Metrohm AG, Switzerland) at room temperature. The CV tests were conducted over the potential window from −0.9 V to 0.9 V at scan rates varying from 5 to 50 mV s^{-1}. The EIS plots were collected with the frequency ranging of 100 kHz –0.01 Hz at an open circuit condition. Galvanostatic charge–discharge cycling tests were recorded between 0 V and 0.8 V at room temperature with a multichannel LAND CT2001A battery tester (Wuhan Landian Electronic Co., China).

3. Results and discussion

The fabrication process of the PPy–RGO-fabric composite is illustrated in Fig. 1a. The raw fabric was first coated with GO via dipping into GO aqueous suspension and subsequent drying. Buglione et al. have demonstrated that the methods used to reduce GO have a dramatic effect on the weight specific capacitance, and that thermally reduced GO exhibited the highest values [31]. Thus, thermal reduction was used in this work because of the excellent stability of cotton fabric under inactive atmosphere [32]. The color changed from brown to light black after reduction (Fig. 1c) due to the restoration of the electronic conjugation. After the deposition of PPy, the fabric turned dark black completely (Fig. 1d). The GO-fabric is not intrinsically conductive. However, the obtained PPy–RGO-fabric is highly conductive and can be used as a textile conductor to join components in a circuit. As shown in Fig. 1e, a red light-emitting-diode was lighted up with the PPy–RGO-fabric serving as a conductor under 3.0 V voltage. The conductivity of the PPy–RGO-fabric was about 1.2 S cm^{-1}, which was comparable to that of the control PPy-fabric (1.2 S cm^{-1}) and the PPy–Cladophora cellulose composite paper (slightly above 1 S cm^{-1}) [33]. The PPy–RGO-fabric still kept good mechanical flexibility of textile (inset of Fig. 1f). The conductance permanence of the PPy–RGO-fabric at different bending states (I–V) was tested *via* measuring the current by using the fabric as a conductor in a circuit at a constant voltage of 0.5 V. For each curvature, the current was recorded for 60 s. It was found that the current was almost unchanged when the PPy–RGO-fabric was bent into different curvatures, indicating that the conductance of the PPy–RGO-fabric was barely influenced by bending.

Fig. 2 shows the SEM images of the RGO-fabric and PPy–RGO-fabric. The fibers presented fairly smooth and neat surface for the raw fabric (inset of Fig. 2a). After dyeing and reduction, RGO coated not only on the surface of the fibers but also filled the interstitial spaces (Fig. 2a). The RGO layer showed a rough and wrinkled surface morphology (Fig. 2b). The compact RGO layer would facilitate ion transportation, possibly giving rise to the improved electrochemical performance. It can be observed clearly that the surface of the RGO-coated fibers became even rough due to the successful attachment of PPy on the surface after chemical polymerization (Fig. 2c). The PPy layer for the PPy–RGO-fabric was consisted of spherical particles in different sizes (Fig. 2d), which was significantly less than that for the PPy-fabric (the inset in Fig. 2d). The mass loading of active materials (the total mass of RGO and PPy) on the PPy–RGO-fabric was only ~1.5 mg cm^{-2}, which was much lower than that on the PPy-fabric (~6.0 mg cm^{-2}) perhaps due to the relatively poorer adsorption of PPy on the