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Wearable supercapacitors on polyethylene terephthalate fabrics with good wash fastness and high flexibility

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HIGHLIGHTS

- The laser-scribed GO layers possess three-dimensionally porous structure.
- As-prepared MSC has high areal specific capacitance and good cycling stability.
- Washing and bending have minimal degradation in MSC's electrochemical performance.
- Cross-linking reaction can improve the wash fastness of all solid-sate MSCs.

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ABSTRACT

All solid-state micro-supercapacitors (MSC) have emerged as attractive energy-storage units for portable and wearable electronics. Here, we describe a textile-based solid-state MSC *via* laser scribing of graphene oxide (GO) coatings on a flexible polyethylene terephthalate (PET) fabric. The laser-scribed graphene oxide layers (LGO) possess three-dimensionally porous structure suitable for electrochemical-double-layer formation. To improve the wash fastness and the flexibility of the as-prepared MSCs, glutaraldehyde (GA) was employed to crosslink the GO layers and PVA-gel electrolyte onto the PET fabric. The resultant all solid-state MSCs exhibited excellent flexibility, high areal specific capacitance (756 $\mu F \cdot cm^{-2}$ at 20 $mV \cdot s^{-1}$), and good rate capability when subject to bending and laundering. Furthermore, the MSC device showed a high power density of about 1.4 $W \cdot cm^{-3}$ and an energy density of 5.3×10^{-5} $Wh \cdot cm^{-3}$, and retained 98.3% of its initial capacitance after 1000 cycles at a current density of 0.5 $mA \cdot cm^{-2}$. This work is the first demonstration of in-plane MSCs on PET fabric surfaces with enhanced durability and flexibility.

1. Introduction

Micro-supercapacitors (MSCs), a group of newly developed miniaturized electronic devices for energy storage, have received considerable attention due to their unique configuration, portability, lightweight and flexibility [1–6]. They also demonstrate higher power density over those of conventional batteries and supercapacitors [7–10]. Many materials have been used to build micro-supercapacitors, including nanostructured carbon-based materials [5,11–15], transition metal oxides [16,17] or sulfides [18], and conducting polymers [19,20]. As the rising star in the carbon family, graphene has played an important role in the construction of in-plan MSCs, as a result of its intriguing properties including excellent electrical conductivity and exceptionally high surface-to-volume ratio [21–28]. For instance, Gao et al. [29] reported the electrochemical performances of laser-scribed GO-based MSCs with both in-plane and sandwich geometries. MSCs with in-plane geometry exhibited higher capacitance density than that of conventional sandwich structure. Wu et al. [30] constructed a planar MSC by using laser carving and electrochemical activating

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of a GO film attached to a flexible polyethylene naphthalate (PEN) substrate. The laser scribing or carving strategies have the advantages of simplicity, low cost and scalability. The resultant MSCs, usually built on flexible substrates, have been reported with light weight and excellent flexibility. Furthermore, MSCs using all-solid-state electrolyte [21] greatly overcome the leaking issues of liquid electrolytes. The widely employed solid-state electrolytes are proton conducting polymer gels, such as PVA/H_2SO_4 [31] and PVA/H_3PO_4 [25,32]. Unfortunately, these solid-state electrolytes are derived from aqueous systems, resulting in poor wash fastness of the resultant MSCs.

Herein, we have developed a solid-state MSC on flexible woven PET fabrics, *via* laser scribing and chemical crosslinking of GO layers and gel electrolytes together with the PET substrate. Glutaraldehyde (GA) has been used as the cross-linker to chemically bind the GO flakes and the solid-state electrolyte (PVA-H_2SO_4) together onto the surface of a PET fabric. Our solid-state MSCs exhibited good electrochemical performance when subject to bending and laundering cycles.

2. Experimental section

2.1. Materials and reagents

Graphite powder (natural flake, 5 μm) was from Asbury Graphite Mill Inc.. Conductive polyvinyl tapes were purchased from Exopack Advanced Coatings. Sulfuric acid (H_2SO_4, 98%, Fisher Scientific), Polyvinyl alcohol (PVA, M_w 89,000–98,000, 99% hydrolyzed, Sigma-Aldrich), and Glutaraldehyde (GA, 25%, Aldrich) were of reagent-grade quality or better and used without further purification. Polyethylene terephthalate (PET) woven fabric with plain weave, 107 g/m^2, warp density 31.5/cm (150 denier) and weft density 21.5/cm (150 denier) was used as a textile substrate.

2.2. Methods

2.2.1. Fabrication process of cross-linked PET-GO-LGO

Graphene oxide (GO) was synthesized from natural graphite powder according to the modified Hummers method [33,34]. To obtain highly cross-linked GO coating on PET fabrics, the GO-GA mixture solution (GO 0.5 wt. %, GA 0.4 wt. %) was first prepared by magnetic stirring (1200 rpm) for 72 h at room temperature. Then, the mixture solution was assembled onto the PET fabric surface by dip-coating method for 30 cycles, resulting in PET-GO-GA. Subsequently, the PET-GO-GA was further cross-linked at 80 °C for 1 h, forming the cross-linked PET-GO (PET-CGO). Finally, PET-CGO-LGO samples were made *via* CO_2 laser scribing of the PET-CGO samples according to the method reported previously [29].

2.2.2. Assembly of in-plane MSCs

The patterned PET-CGO-LGO were covered with the current collector of Au-coated polyvinyl membrane in the same shape as the LGO electrodes. The covered pattern were sandwiched between two glass slides for easy handling. Subsequently, a gel electrolyte of poly(vinyl alcohol) (PVA, 1.0 M)/H_2SO_4 (1.0 M) (PVA-H_2SO_4) was drop-cast onto the device and allowed to solidify overnight. In the second day, the slides were removed from the device and dried at room temperature. To improve the structural integrity of the resulted MSC, PET, CGO, and PVA were further cross-linked with GA (0.4%) *via* dip-coating and drying at room temperature. To evaluate the wash fastness, a typical MSC was exposed to water for 30 min and then dried at ambient conditions. The electrochemical characterization of device performance was executed with devices as-prepared, after cross-linked and washed, and concavely and convexly bent.

2.3. Apparatus

Direct laser scribing was conducted with a CO_2 laser printer (EPILOG Laser Mini Cutter Platform (40 W), scanning speed 30% and power 10%, 2 scribing cycles). Scanning electron microscope (SEM, FEI XHR-Verios 460L), X-ray diffraction (XRD, Anton Parr XRK 900), Fourier transforms infrared spectroscopy (FTIR, Thermo Fisher, Nexus 470, ATR) and Raman spectroscopy (BaySpec Nomadic Raman spectrometer, excitation wavelength 532 nm) were used to characterize the morphology and structure of PET-CGO, PET-CGO-LGO and the resulting in-plane MSCs. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) measurements were used to evaluate electrochemical capacitive performance and performed by an AUTOLAB workstation (PGSTAT302N, Metrohm Autolab, USA). Typically, all the electrochemical measurements were done using 2-electrode system where the alligator clips of the Autolab workstation were directly connected with the two electrodes in our MSCs through current collectors.

3. Results and discussion

Once chemically cross-linked, our in-plane MSCs on PET fabrics exhibited much improved stability and structural integrity against bending and laundering. The details of our prototypes are discussed in the following.

3.1. Fabrication of LGO-based MSCs

Fig. 1 illustrates the process of fabricating our LGO-based MSCs on the surface of a PET fabric. A thin GO-GA film was drop-cast onto the PET fabric from a GO-GA dispersion (GO 0.5 wt. %, GA 0.4 wt. %) (Fig. 1a and b). The resulted PET-GO-GA was further cross-linked at 80 °C for 1 h (Fig. 2a), leading to the cross-linked PET-GO (PET-CGO) (Fig. 1c). After that, the PET-CGO was scribed by a CO_2 laser beam and patterned into microelectrodes in concentric-circular geometry (Fig. 1d) *via* a computer-based programming system. Subsequently, the LGO patterns were covered with the conductive polyvinyl films as the current collectors (Fig. 1e). A polymer gel electrolyte (PVA-H_2SO_4 (1.0 M)) was then drop-cast onto the entire pattern and solidified overnight (Fig. 1f). Notably, the gel electrolyte used here not only avoided the harmful leakage of liquid electrolytes, but also reduced the device thickness by eliminating additional packaging materials. Finally, PET, CGO and PVA were further cross-linked with GA (Fig. 2b), leading to an all solid-state LGO-based MSC (Fig. 1g) on a woven PET fabric. The as-prepared MSC device was tested in two bending modes (concavely bent and convexly bent, Fig. 1h and i).

3.2. Morphology characterization

In sharp contrast to the CGO surface (Fig. 3a), the LGO part shows a clear 3D porous network due to the gas evolution *via* the thermal decomposition of functional groups in GO [35] and intercalated water during localized laser heating (Fig. 3b and c). This unique structure with highly accessible surfaces can facilitate ion transport and diffusion throughout the electrodes and enhance the overall power capabilities of the device. Fig. 3d shows the cross-section of a scribed LGO-CGO-PET structure, highlighting the interfaces between the PET yarns, CGO and LGO structures in a higher magnification, where the orthogonal woven structure of PET fabric can also be clearly observed. Fig. 3e illustrates the profile of a PET-CGO-LGO-based MSC with in-plane geometry. In addition, the LGO electrodes were in good contact with the Au-coated polyvinyl tapes as the current collectors (Fig. 3f).