Improving Performance of Fibriform Supercapacitor Based on Cotton Thread by Uncoiling Dip-Coating Procedure

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Abstract. Fibriform supercapacitor (FSC) based on cotton thread (CT) produced by dip-coating presents great potential in wearable electronics. However, active materials especially for reduced graphene oxide (RGO) sheets tend to restack on the surface of CT and are difficult to permeate into the inside of CT, thus fading performance. In this work, each cotton yarn (CY) obtained by uncoiling CT is uniformly covered by GO (GO-CY) and RGO coated CT (RGO-UCDCT) is obtained through twisting these GO-CYS, followed by subsequent reduction. Uncoiling dip-coating alleviates the restacking of RGO sheets on the surface of CT. Thus, the FSC based on RGO-UCDCTs exhibits superior performance including high volumetric capacitance of 1.85 mF cm$^{-3}$ and good rate capability. The findings provide a cost-effective procedure of uncoiling dip-coating for improving performance of CT based FSC.

1. Introduction

In the latest decades, wearable electronics have been explosively developed as fascinating products. Fibriform supercapacitor (FSC) exhibits a great potential in energy systems for wearable electronics. The common research target on FSC is not only to achieve highly electrochemical performance, but also to realize wearable comfort [1]. The FSC based on cotton thread (CT) substrate presents some unique superiority for realizing the above-mentioned target, such as: (1) CT is comprised of several hanks of cotton yarns (CYS), and each CY is consisted of countless cotton fibers (CFs), thus, active materials with high mass loading can be achieved on CT substrate. (2) CT substrate can provide desired wearable comfort and harmony with textile based clothing. (3) CT is abundant and available, thus, the preparation of FSC based on CT can avoid complex procedures and rigorous conditions.

In consideration of the characteristics of CT including high-porosity and well-hydroscopicity, dip-coating is an effective technique to realize large-scale production for conductive CT electrodes. Graphene oxide (GO) dispersions with features of good stability and mass production show great advantage for fabricating conductive CT using dip-coating technique.

Although preparing RGO coated CT by dip-coating is a cost-effective method, the produced RGO coated CT still has some deficiencies. Typically, the GO sheets tend to concentrate on the surface of CT to form a GO shell during dip-coating process, and the GO shell can further impede the permeation of GO sheets [2, 3]. Therefore, the preparation technique should be improved to solve this problem.

In this work, CT is uncoiled into CYS, which are underwent dip-coating to produce GO coated CYS (GO-CYS). The final RGO coated CT (RGO-UCDCT) is obtained through twisting these GO-CYS,
followed by subsequent reduction. The uncoiling dip-coating procedure not only avoids the restacking of RGO sheets on the surface of CT, but also ensures the uniform distribution of RGO sheets on each CY. Comparing to the directly fabricated RGO coated CT (RGO-CT) without uncoiling dip-coating procedure, the FSC based on RGO-UCDCTs exhibits superior performance.

2. Materials and experimental section

2.1. Materials
CT was purchased from DMC. Each CT contains twelve hanks of CYs, each CY contains countless CFs.

2.2. Experimental details

2.2.1. GO dispersions. GO was synthesized from graphite powder by modified Hummers method [4]. The concentration and pH range of GO dispersions is ~5 mg mL\(^{-1}\) and 2–5.

2.2.2. RGO-UCDCT and RGO-CT. Firstly, CT was uncoiled into CYs. Secondly, GO-CY was prepared by dipping CY into GO dispersions 5 times. Thirdly, GO-CYs were twisted together to form GO-UCDCT and a small quantity of GO dispersions as binder was sprayed on its surface. Finally, RGO-UCDCT was prepared by vapor reduction (RGO: 0.25~0.30 mg cm\(^{-1}\)) [2]. The preparation of RGO-CT is dipping CT into GO dispersions 5 times, followed by vapor reduction (RGO: 0.27~0.33 mg cm\(^{-1}\)).

2.2.3. RGO-UCDCTs based FSC. The PVA-H\(_3\)PO\(_4\) gel electrolyte was synthesized through a reported literature [5]. The FSC was established by twisting two strands of gel electrolyte coated RGO-UCDCTs together. The RGO-CTs based FSC is prepared under the same condition.

2.3. Characterization methods
Gravimetric capacitance (\(C_M\)) of active materials was calculated from cyclic voltammetry (CV) curves based on eqn (1). Volumetric capacitance (\(C_V\)) of FSC device was calculated from CV and galvanostatic charge-discharge (GCD) curves base on eqns (2) and (3), respectively. Volumetric energy density (\(E_V\)) and power density (\(P_V\)) of FSC device were calculated based on eqns (4) and (5), respectively.

\[
C_M = \frac{2\int s V dV}{m A V} \quad (F \text{ g}^{-1}) \tag{1}
\]
\[
C_V = \frac{\int s V dV}{2V_0 A V} \quad (F \text{ cm}^{-1}) \tag{2}
\]
\[
C_V = \frac{\Delta t}{V_0 A V} \quad (F \text{ cm}^{-1}) \tag{3}
\]
\[
E_V = \frac{C_V V_{max}^2}{7200} \quad (Wh \text{ cm}^{-1}) \tag{4}
\]
\[
P_V = \frac{3600E_V}{\Delta t} \quad (W \text{ cm}^{-1}) \tag{5}
\]

Where \(m\) is the mass of active materials in the device (g), \(s\) is scan rate (V s\(^{-1}\)), \(A V\) is potential window (V), \(V_0\) is the total volume of FSC device (the effective length of FSC device is 1~2 cm, the total volumes of FSCs based on RGO-UCDCTs and RGO-CTs are 0.015 cm\(^3\) and 0.016 cm\(^3\)), \(I\) is constant discharge current (A), \(\Delta t\) is discharge time (s) and \(V_{max}\) is operation potential (V).

3. Results and discussion

3.1. Preparation procedures
The preparation of RGO-UCDCT are shown in Fig. 1. Firstly, CT was uncoiled into twelve hanks of CYs (Fig. 1a). Secondly, each CY was dipped into GO dispersions to produce GO-CY (Fig. 1b), and GO-UCDCT was fabricated by twisting these GO-CYs (Fig. 1c). The uncoiling dip-coating procedure can insure the uniform distribution of GO sheets on each CY which even locates in the inner of CT as shown in Fig. 1d. Thirdly, a small quantity of GO dispersions as binder was sprayed on the surface of GO-UCDCT. After drying, the sprayed GO dispersions can form a layer of GO shell which can fix the
intertwined GO-CYs (Fig. 1e). Finally, RGO-UCDCT was produced by vapor reduction. As show in Fig. 1f, a strand of 1 m long RGO-UCDCT with metallic luster was coiled on the bobbin.

Figure 1. (a) Uncoiling CT into CYs. (b) GO-CY. (c) Twisting GO-CYs into GO-UCDCT. (d) GO-UCDCT. (e) GO-UCDCT covered by a layer of GO shell. (f) RGO-UCDCT.

GO-CT was prepared by directly dipping bare CT (Fig. 2a) into GO dispersions without uncoiling dip-coating procedure. As shown in Fig. 2b, GO-CT presents a color of brownish yellow, however, some of the CYs located in the inner of GO-CT present the colors of faint yellow and white. The uneven distribution of GO is caused by two factors: (1) the CYs located in the periphery of CT closely arrange to form a surface like a substrate, and GO sheets tend to attach to this surface to form a layer of GO shell. (2) More and more GO sheets attach to this layer of GO shell and cannot permeate into the inner of CT. The inconspicuous metallic luster of RGO-CT (Fig. 2c) may be caused by the limited reduction because of the thick layer of GO shell.

Figure 2. (a) Bare CT. (b) GO-CT. (c) RGO-CT.

3.2. Morphology, structural defect and chemical composition analyses
The SEM images of RGO-UCDCT and RGO-CT are shown in Fig. 3a-d and e-h. The outlines of CYs can be faintly seen in RGO-UCDCT (Fig. 3a) due to the small thickness of RGO shell. The CFs in RGO-UCDCT compactly arrange (Fig. 3a, b) while the CFs in RGO-CT distribute unevenly (Fig. 3e,f). The large interspaces existed in RGO-CT (the black regions in Fig. 3f) indicate that few of GO sheets
permeate into the inner of CT. The outlines of CFs located in the central region of RGO-UCDCT show irregular shapes with plenty of RGO fragments (Fig. 3c), demonstrating that the uncoiling dip-coating improves the permeation of GO sheets into the inner of CT. However, the outlines of CFs located in the central region of RGO-CT is smooth (Fig. 3g), further implying that few of RGO sheets coat on these CFs. In addition, the RGO shell on the surface of RGO-UCDCT is thin with layered structure (Fig. 3d), which is attributed to the controllable spray-coating and completely reduction. As a contrast, the RGO shell on the surface of RGO-CT is significantly thick without layered structure (Fig. 3h).

Raman spectra exhibit D peak at 1342 cm\(^{-1}\) and G peak at 1589 cm\(^{-1}\) (Fig. 3i). The larger \(I_D/I_G\) of RGO-UCDCT (1.77) compared to that of RGO-CT (1.45) is attributed to the enlarged disordered degree of RGO sheets with improved reduction degree. Compared with RGO-CT, RGO-UCDCT exhibits the increased C1s peak while decreased O1s peak (Fig. 3j) because of the high-level reduction. Additionally, RGO-UCDCT reveals the significantly decreased oxygen peaks compared with RGO-CT (Fig. 3k). The surface C/O atomic ratio detected by XPS are ~5.28 for RGO-UCDCT and ~4.51 for RGO-CT. These results further demonstrate that the reducibility vapor flow can effectively convert the thin layer of GO shell into RGO and permeate into the inner of GO-UCDCT to conduct reduction reaction.

3.3. Electrochemical performance analysis

CV curves with quasi-rectangular shapes (Fig. 4a) and GCD curve with nearly symmetric triangle (Fig. 4b) are characters of good electric double layer capacitive behavior [6]. The larger CV loop (Fig. 4c) and longer discharge time (Fig. 4d) of FSC based on RGO-UCDCTs compared to those of FSC based on RGO-CTs indicate improved specific capacitance. Typically, FSC based on RGO-UCDCTs exhibits \(C_F\) of 1.85, 1.45, 1.18, 1.04, 0.96 and 0.93 mF cm\(^{-1}\) at scan rates of 50, 100, 200, 300, 400 and 500 mV s\(^{-1}\), which are higher than those of FSC based on RGO-CTs (0.78–0.33 mF cm\(^{-1}\)) at the same scan rate range (Fig. 4e). FSC based on RGO-UCDCTs also exhibits superior rate capability of 50.3% capacitance retention compared to FSC based on RGO-CTs (42.3%). In addition, RGO in RGO-UCDCT exhibits \(C_m\) of 123.3 mF g\(^{-1}\) at 50 mV s\(^{-1}\), 146% higher than that of RGO in RGO-CT (50.2 mF g\(^{-1}\)). Due to the superior \(C_F\), the FSC based on RGO-UCDCTs provides a higher \(E_V\) of 0.077 μWh cm\(^{-3}\) compared to
FSC based on RGO-CTs (0.053 $\mu$Wh cm$^{-3}$) at the same $P_V$ of 50 $\mu$W cm$^{-3}$. The intercept of Nyquist plot (Fig. 4f) on real axis denotes equivalent series resistance (ESR). The FSC based on RGO-UCDCTs exhibits the lower ESR of 1.92 k$\Omega$ than FSC based on RGO-CTs (4.32 k$\Omega$).

The improved electrochemical performance of FSC based on RGO-UCDCTs is ascribed to the following reasons: (1) the uncoiling dip-coating procedure effectively avoids the serious restacking of RGO sheets on the surface of CT and enhances the utilization rate of active materials, eventually resulting in the improved $C_M$ and $C_V$. (2) High level reduction and uniform distribution of RGO sheets in RGO-UCDCT electrode are beneficial for constructing the developed conductive network for ion and electron transport, thus achieving the superior rate capability.

4. Conclusion
In summary, high performance RGO-UCDCT electrode is successfully fabricated by uncoiling dip-coating procedure. In RGO-UCDCT, each CY is uniformly covered by RGO sheets which is beneficial for constructing the developed conductive network. Meanwhile, the uncoiling dip-coating avoids the serious restacking of RGO sheets on the surface of CT. Thus, the FSC based on RGO-UCDCTs exhibits extraordinary electrochemical properties and great potential for application in wearable electronics.

Acknowledgments
We are grateful to the National Natural Science Foundation of China (Grant Nos. 51773027 and 21572030) and National Key R@D Program of China (No. 2017YFB0702800) for financial support.

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