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Electrodeposition of polypyrrole on carbon nanotube-coated cotton fabrics for all-solid flexible supercapacitor electrodes

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Abstract: The increasing trend of portable and wearable electronic products requires the development of portable and flexible energy-storage systems, such as flexible supercapacitors. We have attached polypyrrole and carbon nanotube on cotton fabrics as electrodes to prepare all-solid, flexible supercapacitors. Since the substrate is cotton, the supercapacitor is comfortable when worn and when in contact with the skin. Electrochemical measurements showed that the supercapacitor had a specific capacitance of 201.99 F g\(^{-1}\) at 1.8 A g\(^{-1}\). Its high capacitance, stability, flexibility, low-cost, and wearing comfort make this supercapacitor a good candidate as an energy-storage device for portable and wearable electronic products.

1. Introduction

Supercapacitors have generated interest as a novel energy storage device because of their higher power density over traditional batteries, longer cycling stability, and higher energy density than conventional capacitors.\(^1\)\(^-\)\(^6\) However, traditional supercapacitors are rigid and do not satisfy human requirements. Societal developments have led to demands for lightweight, portable, and flexible electronics, such as paper-like mobile phones, wearable electronics and other easily collapsible gadgets. Next-generation supercapacitors are expected to become flexible, environmentally friendly energy storage devices.\(^7\)\(^-\)\(^10\)

Carbon nanotube (CNT) is a novel carbon material and has shown great potential in supercapacitor devices.\(^11\)\(^-\)\(^14\) CNT has a one-dimensional tube-like structure with outstanding electrical properties and excellent flexibility, which makes them suitable as the backbone of flexible electrodes. A thin-film CNT as substrate meets requirements of high conductivity, flexibility, and long cycling stability in the development of flexible supercapacitors. However, its low specific capacitance limits its application in supercapacitor devices.\(^15\)\(^,\)\(^16\) The combination of conducting polymer and CNT is an effective method to obtain supercapacitor with large capacitance, good rate capability, superior stability, and outstanding flexibility.\(^17\)\(^-\)\(^20\) Polypyrrole (PPy) is considered to be a promising material for supercapacitor owing to its high electrical conductivity, high energy storage capacity, low cost, simple synthesis, and benign environmental properties among conducting polymers.\(^21\)\(^,\)\(^22\)

In recent years, various methods have been developed to fabricate PPy/CNT and PPy/reduced graphene oxide (RGO) composites, including surface coating through in-situ, chemical oxidative, and electrochemical polymerization.\(^23\)\(^-\)\(^27\) However, it is difficult, environmentally unfriendly, and costly to fabricate CNT or RGO films with large area. Cotton fabrics are used extensively in clothing, industry, and agriculture, and are lightweight, wearable, flexible, highly porous, and elastic. Cotton fabrics could serve as ideal substrates for flexible electric devices when coated with conducting materials.\(^28\)\(^,\)\(^29\) For example, carbon materials and conducting polymers can be attached on the cotton fabrics by printing technologies, 3D printing, or situ chemical polymerization, etc.\(^30\)\(^-\)\(^35\)

In this study, CNT was loaded on cotton fabric substrates via ultrasonic dispersion and PPy was deposited on the CNT/cotton fabrics by electrochemical methods. As PPy was directly electrochemical deposited on CNT, better combination can be formed between them, which will benefit the electron transport during charge/discharge process. Besides, this approach is low cost (the concentration is only 0.28 M and don’t need any oxidant), simple (short time and the reaction can be easily controlled by potential), and environmentally friendly (the electrolyte is aqueous solution). The combination of PPy/CNT/cotton fabric electrodes can provide a high power density, flexibility, wearability, and environmental friendly for energy storage.

2. Experimental section

2.1 Preparation of CNT/cotton fabric
Cotton fabrics were obtained from T-shirts, and were washed with ethanol to remove impurities before use. CNT (Multi-wall carbon nanotube, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China) was dispersed in absolute ethanol, two pieces of cotton fabrics (0.5 cm × 1.5 cm) were stitched together and immersed into CNT dispersion (4.0 mg/mL), and the mixture was treated under ultrasonic conditions for 6.0 h. Strips of cotton fabric were removed from the CNT dispersion, washed with absolute ethanol, and dried for 24 h in air at room temperature. The cotton fabric changed from white to black, which indicates that CNT was loaded on the fabric stably. The conductive composites were termed CNT/cotton fabric.

2.2 Preparation of PPy/CNT/cotton fabric

Flexible PPy/CNT/cotton fabric was prepared by electropolymerization of PPy film on CNT/cotton fabrics, which was carried out at room temperature in a one-compartment cell using an electrochemical workstation (CHI600E, Shanghai Chen Hua Instrument Co., China) under computer control. The CNT/cotton fabric was used as the working electrode, the counter electrode was a platinum coil, and all potentials were referred to a saturated calomel electrode. The electrolyte was an aqueous solution containing pyrrole (0.28 M, Sinopharm Chemical Reagent Co., China) and lithium perchlorate (0.07 M, Sinopharm Chemical Reagent Co., China), which was degassed with nitrogen before polymerization. A PPy film was formed on the CNT/cotton fabric electrode surface. The time for PPy film formation was varied from 200 to 800 s. The applied potential was varied from 0.80 to 0.90 V. The as-prepared flexible composites of PPy/CNT/cotton fabric were rinsed with deionized water and dried for 24 h in air at room temperature before characterization.

2.3 Fabrication of supercapacitors

The two stitched nearly identical pieces of composite films were taken apart (5 mm × 5 mm) and used as electrodes. H₃PO₄/polyvinyl alcohol (PVA) (Sinopharm Chemical Reagent Co., China) electrolyte were dropped on the surface of the films. Then the two pieces of films were overlapped with electrolyte sandwiched between them. After they were dried at room temperature for 12 h, an all-solid supercapacitor was formed. The dried electrolyte could make the two films stick to each other, and the entire device could be bent without obvious delamination.

2.4 Characterization and measurements

Sample morphology was studied by field-emission scanning electron microscopy (SEM, Ultra55, Carl Zeiss SMT Pty Ltd, Germany). Fourier-transform infrared spectroscopy (FTIR, 0.09/cm/Nicolet 5700, Thermo Electron Corporation, USA) and Raman spectra (TriVista TR557, Princeton Instruments, λ = 488 nm, USA) were used to characterize the molecular structure of the PPy products. Sample electrochemical performance was examined by cyclic voltammetry (CV), galvanostatic charge–discharge, and impedance spectra using the same electrochemical workstation as above.
3. Results and discussion

Figure 1 shows a schematic illustration of the preparation of the supercapacitor process. CNT was loaded on cotton fabric by dipping and ultrasonic dispersion as substrates. PPy was deposited on CNT/cotton fabric by electrochemical methods. The supercapacitor was formed by two nearly identical pieces of composite electrodes, which were overlapped and separated by H$_3$PO$_4$/PVA electrolyte.

Figure 2a and 2b shows the SEM images of cotton fabric. It can be seen that the cotton fabric are made of a large number of cotton fibers with numerous gaps between the fibers. Therefore, CNT can enter into the space between the fibers. Figure 2c-f shows SEM images of the CNT/cotton fabric and PPy/CNT/cotton fabric surface at different magnifications. Cotton fabric fibers were encased in CNT, and the fiber surface became rough (Figures 2c and 2d). As shown in Figure 2f, the CNT surface became rough compared with Figure 2d. Furthermore, the CNT diameter in the PPy/CNT/cotton fabric composite is slightly larger after coating with PPy via electrochemical polymerization. The chronoamperometric curves of electrochemical polymerization are shown in Figure S1. The SEM images in Figures S2 and 2f, show that the CNT surface became rougher with increase in reaction time from 200 to 600 s, which indicates that the PPy films were deposited uniformly on CNT/cotton fabrics by electrochemical methods.

The chemical structure of the cotton fabric, CNT/cotton fabric and PPy/CNT/cotton fabric (0.85 V, 600 s) was determined by reflectance FTIR spectroscopy. The characteristic cotton fabric peaks are shown in Figure S3. However, the IR spectra of CNT/cotton fabric had no obvious characteristic peaks, which implies that the cotton fabric surface is covered entirely by CNT. As shown in Figure 3a, the IR spectra of the PPy/CNT/cotton fabric show characteristic PPy peaks, such as symmetric ring stretching at 1460 cm$^{-1}$, C-N stretching vibration at 1311 cm$^{-1}$, and C-H deformation vibrations at 1032 cm$^{-1}$. Figure 3b compares Raman spectra before and after coating of PPy film onto CNT/cotton fabric. The characteristic peak centered at 1552 cm$^{-1}$, which corresponded to the Raman phonon vibration of the CNT G-band. The D-band was disappeared after CNT was load on cotton fabric, which may be due to the adsorption effect between CNT and cotton fabric. The G-band intensity decreased after coating of the PPy film.

![Figure 3](image-url)

**Figure 3.** FTIR spectra (a) and Raman spectra (b) of CNT/cotton fabrics and PPy/CNT/cotton fabrics.

![Figure 4](image-url)

**Figure 4.** (a) CV curves of CNT/cotton fabric and PPy/CNT/cotton fabric supercapacitor. (b) Galvanostatic charge–discharge curves at current densities of 1.8 A g$^{-1}$. (c) Nyquist plot of PPy/CNT/cotton fabric supercapacitor.
The electrochemical performance of PPy/CNT/cotton fabric supercapacitor was evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge in a two-electrode configuration. The performance of the CNT/cotton fabric supercapacitor was also evaluated for comparison. As shown in Figure 4a, the CV curve of PPy/CNT/cotton fabric supercapacitor had a large enclosed area and a good symmetrical rectangular shape, which indicates the ideal pseudocapacitive nature of the PPy/CNT/cotton fabric and the fast redox reaction with a solid H$_3$PO$_4$/PVA electrolyte. In general, the enclosed area of the CV curve is proportional to the specific capacitance of the electrode material.\textsuperscript{40} For example, the area-specific capacitance (C\textsubscript{a}) can be calculated from C\textsubscript{a} = Q/A × ∆U,\textsuperscript{41} where A is the electrode area, ∆U is the potential window, and Q is the charge, which is proportional to the enclosed area of CV curve. The calculated C\textsubscript{a} of CNT/cotton fabric and PPy/CNT/cotton fabric supercapacitor is 4.45 mF cm\textsuperscript{-2} and 50.09 mF cm\textsuperscript{-2} at 25 mV s\textsuperscript{-1}, respectively. By comparing the value of C\textsubscript{a}, it can be seen that a combination of PPy and CNT improves the capacitance compared with CNT only, which can be explained by the combined contributions from the high pseudocapacitance of PPy and the high conductivity of CNT.

The galvanostatic charge–discharge curve of the PPy/CNT/cotton fabric supercapacitor at a constant current of 1.8 A g\textsuperscript{-1} was linear (Figure 4b), which indicates a good device capacitance performance. The mass specific capacitance was 201.99 F g\textsuperscript{-1} as calculated from:

$$C_p = \frac{2Q}{(\Delta V \times m)} = \frac{(2I \times t)}{(\Delta V \times m)}$$

where I represents the constant discharge current, t is the discharging time, m is the mass of one electrode, and ∆V is the voltage drop on discharging. The power and energy density were 64.64 Wh kg\textsuperscript{-1} and 5.14 kW kg\textsuperscript{-1}, respectively.

As shown in Figure 4c, Nyquist plot was obtained in the frequency range from 100 kHz to 0.1 Hz. In the low-frequency portion of the plot, the curves tend towards a vertical line, indicating that the supercapacitors show good capacitive behavior and good ion diffusion in the electrode structure.

The relationship between the electrodeposition time, electrodeposition potential, and the device performance was
studied by CV. As illustrated in Figure 5a, a constant potential for PPy electrodeposition of 0.85 V was used, and the deposition time was from 200 to 800 s. All CV curves were conducted at a scan rate of 25 mV s\(^{-1}\), but their enclosed area had obvious differences. The value of \(C_a\) increases with increase in electrodeposition time and reaches a maximum, which shows that the capacitive behavior of the device could improve significantly by optimizing the PPy electrodeposition time. However, \(C_a\) decreases slightly when the electrodeposition time is greater than 600 s. Because, the doping/dedoping of PPy can easily be carried out on the surface, too much loaded PPy would decrease the specific surface area. Additionally, as the conductivity of CNT (\(<100 \text{ s cm}^{-1}\)) is much higher than that of PPy (\(<1 \text{ s cm}^{-1}\)) and electrons must transport from PPy to CNT during charge/discharge process, too much PPy means much longer transport route for electron, which may reduce the performance of supercapacitor. This result is consistent with literature reports.\(^{4,43}\) The study also used a constant 600 s electrodeposition time, and the PPy deposition potential was from 0.80 to 0.90 V. The CV curves corresponding to different deposition potentials are shown in Figure 5b, and CV curves were obtained at a scan rate of 25 mV s\(^{-1}\). The result and reasons are the same as those in Figure 4a; \(C_a\) also reaches a maximum, and decreases slightly when the electrodeposition potential is higher than 0.85 V. In our study, composites of PPy/CNT/cotton fabric (600 s, 0.85 V) were chosen as electrodes to provide the capacitors with a relatively high capacitance and rapid charge–discharge capacity.

Cycling stability of the supercapacitors was tested by long-term CV, as shown in Figure 5c. The capacitance increased during the first 260 cycles and then decreased. The capacitance retention after 260 cycles was 179%. Such an increase in capacitance can be attributed to changes in active material microstructure during cycling.\(^44\) The capacitance retention after 375 and 400 cycles was 93 and 87%, respectively. However, the capacitance then decreased rapidly. Only \(~50\%\) capacitance was preserved after 500 cycles. The supercapacitor cycling stability was not very good. More effort is underway to improve the cycling property by optimizing the structure of the electrodes or developing new stable composites. However, because of its low cost and facile preparation, it shows promising application in wearable electronic products in modern times when apparel needs to be changed rapidly to keep up with fashion trends.

In practical applications, portable and flexible electronics may require highly flexible power sources working at different deformation. Figures 6a show the excellent flexibility and good mechanical properties of the thin film electrodes, which can be bent and folded. A supercapacitor was assembled from two PPy/CNT/cotton fabric electrodes and H\(_3\)PO\(_4\)/PVA electrolyte. The as-fabricated supercapacitor is lightweight, highly flexible, and can be twisted and rolled up without destroying the structural integrity of the device (Figures 6b and 6c). Figure 6d shows that the area-specific capacitances were almost unchanged after bending (surrounding a cylinder of 1.5 cm diameter). We repeated the bending study 50 times, and obtained an average decrease of 2%.

To estimate the reliability after continuous bending, the flexible PPy/CNT/cotton fabric planer supercapacitor was tested after 400 bending cycles with 180° bending angle. As shown in Figure 6e, the CV curve after 200 and 400 bending cycles decreased by 17% and 24% relative to the initial curve, respectively, which demonstrates good mechanical robustness.

4. Conclusions

Flexible PPy/CNT/cotton fabric electrodes were synthesized via ultrasonic and a simple electrochemical method for the preparation of flexible supercapacitors. The use of textiles to manufacture flexible supercapacitors is low cost, environmentally friendly and simple. The PPy/CNT/cotton fabric supercapacitors were lightweight, highly flexible, showed good stability, had a high specific capacitance (~201.99 F g\(^{-1}\) at 1.8 A g\(^{-1}\) or 50.09 mF cm\(^{-2}\) at 25 mV s\(^{-1}\)), and are promising for use in various power-wearable electronics.

We also studied nonwoven fabrics (NWF), which formed PPy/CNT/NWF composites under the same conditions, to replace cotton fabrics. The electrochemical behavior of PPy/CNT/NWF is shown in Figures S4 and S5, and its specific capacitance is ~6.80 mF cm\(^{-2}\)at 25 mV s\(^{-1}\). Thus, the performance of the PPy/CNT/NWF supercapacitors is poorer than that of the PPy/CNT/cotton fabrics.

For mass market applications, more effort will be made to realize the large areas and big numbers of cotton-substrated supercapacitors in short time by alternating the manufacturing step, e.g. mass printing technologies instead of electrochemical deposition.

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