Flexible supercapacitor with a record high areal specific capacitance based on a tuned porous fabric†

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To meet the rapidly growing demand for wearable electronics, much research has been devoted to developing flexible supercapacitors. Now, we are awash with abundant examples, but there remain challenges associated with obtaining a high loading of active material for high areal specific capacitance. Herein, a tuned porous fabric has been designed as the substrate to incorporate active materials with a high loading capability. A conducting polymer of polypyrrole with a high mass loading of 12.3 mg cm⁻² was developed, and a record high areal specific capacitance of 4117 mF cm⁻² has been achieved in the resulting supercapacitor. The supercapacitor is also flexible, and it maintains a high electrochemical performance under bending and twisting for 500 cycles.

Introduction

Wearable electronics have gained much attention and will soon become part of our daily life, e.g., in the fields of healthcare, entertainment, sports and communications.¹–³ Among several obstacles in the development of wearable electronics, constructing flexible energy storage devices has become one of the most pressing issues.⁴–⁶ Supercapacitors represent a promising candidate, due to their high power density and durable longevity.⁷ Therefore, much effort has been devoted to making flexible supercapacitors.⁸ To this end, it is critical to develop flexible electrodes that generally consist of electrochemically active materials, conductive additives and binders for high energy storage capability.⁹–¹¹

Conducting polymers are the most commonly explored material for use as flexible electrodes in supercapacitors.⁷,¹¹–¹⁶ To enhance the loading capability of a conducting polymer, a variety of porous substrates have been developed to load conducting polymers, e.g., foams and fabrics.¹⁷–²⁰ Although some significant progress has been made, several critical challenges remain that need to be addressed urgently. Firstly, mass loadings have generally been lower than 6 mg cm⁻² (Table S1 and Fig. S1†), while the commercial requirement is higher than 10 mg cm⁻².²¹ Secondly, a rapid decrease in specific capacitance has been observed with an increase in mass loadings,²²,²³ e.g., from 1023 to 440 F g⁻¹ upon an increase in polyaniline loading from 0.47 to 4.7 mg cm⁻².²⁴,²⁵ Thirdly, the electrochemical performance of these polymers has been reported to be unstable under bending and twisting at high mass loadings.²⁶ The key problem lies in the lack of a systematic study to design and optimize the porous substrate. The emphasis has been persistently on investigating the morphology of the active materials.²²,²⁷,²⁸ However, the porosity and pore configuration of the porous substrate also play critical roles in the incorporation of the conducting polymer, and it is necessary to understand their impact in order to obtain high electrochemical performances.

Herein, a variety of flexible fabrics based on cellulose fibers has been developed with both tunable porosity and pore configuration by controlling the fabric construction. A high porosity of 80% with an average pore diameter of 45 µm was obtained after optimization. Polypyrrole (PPy) was then deposited and polymerized on the fabrics to create flexible electrodes with mass loadings of up to 12.3 mg cm⁻², and the areal specific capacitance reached a record high of 4117 mF cm⁻². The resulting supercapacitor was flexible and could operate effectively during and after bending or twisting for 500 cycles.

Experimental section

Deposition of PPy

A fabric was first immersed into an aqueous solution with anthraquinone-2-sulfonic acid (AQSA) and pyrrole. The
concentration of pyrrole was varied from 0.01 to 0.22 mol L\(^{-1}\), which determined the mass of the deposited PPy. The solution was kept at 0°C and stirred for 10 min. Then a FeCl\(_3\) aqueous solution was added dropwise to initiate polymerization. The molar ratio of pyrrole/FeCl\(_3\)/AQSA was 1/2/0.25. The polymerization reaction lasted for 90 min at 0°C. Finally, the PPy-coated fabric was obtained, washed with water to remove impurities and the separable PPy particles, and afterwards dried in an oven at 100°C. The PPy-coated fabric obtained could be directly used as an electrode. Generally, 50 mL of pyrrole solution was used per 1 g of bare fabric.

**Composition, structure and morphology characterization**

The composition, structure and morphology were characterized using X-ray diffraction (XRD, Bruker, D8 ADVANCE), scanning electron microscopy (SEM, Hitachi, S-4800), Fourier transform infrared spectroscopy (FTIR, Nicolet, 6700) and energy dispersive spectroscopy (EDS, Oxford, X-Max\(^{x}\)). Pore sizes and pore size distributions of the bare and PPy-coated fabrics were measured using a bubble-point method on a capillary flow porometer (CPF, PMI, 1100A). The samples with an area of 9 cm\(^2\) were first wetted by a porometer wetting fluid (Quantachrome Instruments, Porofil\(^{tm}\)) and then sealed in the test cell. When the gas pressure exceeded the capillary trapping force between the wetting agent and the fabric surface, the compressed air passed through the sample gradually. The pore sizes could be calculated by using the following equation:

\[
r = \frac{2y}{\Delta P}\cos \theta
\]

where \(r\) is the radius of the pore, \(\Delta P\) is the pressure difference, \(\gamma\) is the surface tension of the wetting agent and \(\theta\) is the wetting angle. The specific surface area of the fabrics was measured using the Brunauer–Emmett–Teller (BET) method during adsorption. The fabrics were cut into small pieces and the samples were kept under vacuum at 60°C overnight to outgas any pre-sorbed chemicals. Adsorption isotherms were obtained using a gas sorption analyzer (Quantachrome Instruments, Autosorb-iQ). The adsorbate gas, krypton (Kr, 99.999%), was used instead of N\(_2\) because the specific surface areas of the fabrics were less than 5 m\(^2\) g\(^{-1}\).

**Electrochemical measurements**

A standard three-electrode system was used to measure the electrochemical properties of the PPy-coated fabric, using 1 M H\(_2\)SO\(_4\) as the electrolyte and a Pt sheet, Ag/AgCl and PPy-coated fabric as the counter, reference and working electrodes, respectively. The voltage window was varied from −0.3 to 0.5 V (vs. Ag/AgCl), and the current densities were varied from 2 to 20 mA cm\(^{-2}\). For the supercapacitor composed of two PPy-coated fabrics, the voltage window was ranged from 0 to 0.8 V and a gel electrolyte was used. To prepare the gel electrolyte, water (10 mL) and phosphoric acid (10 mL) were mixed and stirred for 30 min. A PVA power (10 g) was dissolved in 90 mL of water at 90°C and then added to the above solution under stirring for 1 h, followed by cooling to room temperature. For the PPy-coated fabric, the capacitance (\(C_1\)) was calculated from the galvanostatic charge/discharge test using the equation:

\[
C_1 = \frac{2 \times I \times \Delta t}{\Delta U}
\]

where \(I\), \(\Delta t\) and \(\Delta U\) correspond to the discharge current, discharge time and voltage window, respectively. The areal specific capacitance (\(C_a\)) and volumetric specific capacitance (\(C_v\)) were obtained from dividing \(C_1\) by the area and volume of the PPy-coated fabric, respectively. The gravimetric specific capacitance (\(C_m\)) was computed from dividing \(C_1\) by the mass of PPy. As for the supercapacitor, the capacitance (\(C_v\)) was also calculated from the galvanostatic charge/discharge test, based on the equation:

\[
C_v = \frac{I \times \Delta t}{\Delta U}
\]

The energy density (\(E_m\)) of the supercapacitor was calculated from the equation:

\[
E_m = \frac{C_v \times U^2}{3.6 \times M}
\]

where \(M\) is the total mass of the two electrodes. The power density (\(P_m\)) of the supercapacitor was then obtained from the equation:

\[
P_m = \frac{E_m \times 3600}{\Delta t}
\]

**Results and discussion**

Fig. 1a illustrates the fabrication process of the fabric electrode. Cellulose fibers with an irregular section (Fig. S2\(^{\dagger}\)) were made into fabrics. Here, three fabric constructions were used with different porosities and pore configurations, i.e., knitted, woven and nonwoven structures (Fig. 1b–d). After polymerization, PPy was uniformly coated onto the surface of the fibers in the fabric.

The knitted, woven and nonwoven fabric templates are shown in Fig. 2a–c and compared using the pore size distribution test. It was found that the knitted fabric possessed a porosity of 80% and pore sizes ranging from 5 to 115 μm, with an average pore diameter of 45 μm (Fig. S3a\(^{\dagger}\)). The woven fabric exhibited a porosity of 68% and pore sizes ranging from 1 to 50 μm, with an average pore diameter of 11 μm (Fig. S3b\(^{\dagger}\)). The nonwoven fabric displayed a porosity of 84% and pore sizes ranging from 20 to 125 μm, with an average pore diameter of 50 μm (Fig. S3c\(^{\dagger}\)). The fabric structure was critical to the porosity and pore sizes, which would in turn determine the
The loading of PPy. The specific surface areas were measured to be 1.05, 0.76 and 1.11 m² g⁻¹ for the knitted, woven and nonwoven fabrics, respectively.

The bare and PPy-coated cellulose fibers in the knitted fabric are compared in Fig. 2d–f. For the bare cellulose fibers in Fig. 2d, a groove (a characteristic of cellulose fibers), can be clearly observed. This gradually disappeared after the deposition of PPy. The deposited PPy layer was smooth, even at a high PPy mass loading of 12.3 mg cm⁻² (Fig. 2e and f). It can be understood that the PPy layer is constructed by the stacking of PPy nanoparticles (Fig. S4†), uniformly coating the fiber (Fig. S5†). PPy was also found to be effectively coated on the cellulose fibers in the woven and nonwoven fabrics (Fig. S6†). The PPy layer was also smooth and uniform for the nonwoven fabric at a high PPy mass loading of 7.17 mg cm⁻² (Fig. S6e and f†), but small PPy aggregates, typically with diameters of hundreds of nanometers, formed when the PPy mass loading reached 5.88 mg cm⁻² in the woven fabric (Fig. S6c†). Therefore, the knitted and nonwoven structures were better suited to PPy deposition compared with the woven structure. Additionally, the thicknesses of the three types of fabric were the same, at nearly 1 mm (Fig. S7a†), and this slightly increased after PPy deposition (Fig. S7b†).

The effective deposition of PPy on the fabrics was further verified by FTIR (Fig. S8†), XRD (Fig. S9†) and EDS (Fig. S10†). The FTIR spectra for the bare and PPy-coated fabrics are shown in Fig. S8†. For the bare cellulose fibers, the peaks at 1033, 1055 and 1106 cm⁻¹ are assigned to ν(C–O) vibrations in alcohol (R–OH) groups;²⁹ the peaks at 1157, 1203 and 1276 cm⁻¹ are ascribed to ν(C–O) vibrations in ester, ether and phenol groups, respectively; the peaks at 1313, 1365 and 1427 cm⁻¹ are

![SEM images of the fabric electrodes. (a) Knitted fabric. (b) Woven fabric. (c) Nonwoven fabric. (d–f) Knitted fabrics coated by PPy with increasing mass loadings of 0, 6.6 and 12.3 mg cm⁻², respectively.](image)

![Fig. 3](image)
attributed to $\nu$(C–O) stretching in carboxylic groups; the peak at 1639 cm$^{-1}$ comes from $\nu$(C–C) vibrations in alkene groups.$^{30}$ For the PPy-coated cellulose fibers, the peaks at 1159 and 1313 cm$^{-1}$ are assigned to the ring-stretching of PPy and C–N stretching vibrations, respectively; the peaks at 1452 and 1542 cm$^{-1}$ are assigned to the backbone stretching vibrations of C–C and C–C in the PPy rings, respectively.$^{23}$ For the XRD spectrum (Fig. S9†), the diffraction peaks at around 15.6°, 22.5° and 34.2° (marked with *) are attributed to cellulose.$^{32}$ After the deposition of PPy, the intensity of the cellulose peaks was reduced and a broad peak centered at 26.7° appeared, which is assigned to PPy.$^{33}$ From the EDS characterization (Fig. S10†), the elements of C, O and N were found to be uniformly distributed on the fiber.

The concentration of pyrrole played a critical role in the polymerization (Fig. 3a). For the knitted fabric, the PPy mass loading was increased as the pyrrole concentration increased up to 0.2 mol L$^{-1}$ and was then slightly reduced beyond this point. The mass loading reached a maximum at 12.3 mg cm$^{-2}$. For the woven and nonwoven fabrics, the PPy mass loading also first increased and then decreased with increasing pyrrole concentration, but critical concentration points were noted at 0.16 and 0.2 mol L$^{-1}$, respectively. Accordingly, the maximal mass loadings were 5.88 and 7.17 mg cm$^{-2}$. The electrical resistivity was an important parameter for the performance of the electrodes (Fig. 3b). The sheet resistance in all fabrics decreased when the PPy mass loading increased. When the mass loading exceeded 6 mg cm$^{-2}$, the sheet resistance was less than 50 Ω $\square$ $^{-1}$, which makes these materials competitive compared to other electrodes.$^{34,35}$

The dependence of the areal specific capacitance on the pyrrole concentration was then carefully investigated (Fig. 3c). The maximal areal specific capacitances for the knitted, woven and nonwoven fabrics were calculated as 4117, 2191 and 2905 mF cm$^{-2}$, respectively. The areal and gravimetric specific capacitances for the three kinds of fabric were compared under increasing PPy mass loading (Fig. 3d). The gravimetric specific capacitances typically varied between 300 and 450 F g$^{-1}$. For instance, the values were 391, 418, 440, 427 and 335 F g$^{-1}$ at PPy mass loadings of 0.42, 2.11, 6.60, 7.96 and 12.3 mg cm$^{-2}$, respectively (Fig. 3d). The slightly decreased gravimetric specific capacitances at high mass loadings exceed most of the previous systems.$^{21-23}$ As for the PPy-coated knitted fabric, the volumetric specific capacitance reached a maximum at 41.17 F cm$^{-3}$, taking into account a thickness of 1 mm (Fig. S7†).

A direct observation of the polymerization process is shown in Fig. S11†. Pyrrole tends to polymerize on the fibers in the fabric due to physical adsorption (Fig. S11b–d).$^{36}$ For the woven fabric, the pyrrole solution became dark after a short period of polymerization (Fig. S11c†), revealing that the woven fabric has a low loading capacity. For the nonwoven fabric, the pyrrole solution became dark after an ultrasonic treatment (Fig. S11f†), illustrating that the PPy layer can become detached, leading to a low effective mass loading. As for the knitted fabric, most of the pyrrole is polymerized on the fibers and shows good bonding, resulting in a high resultant mass loading (Fig. S11b and e†). This phenomenon is consistent with the results of the mass loading test (Fig. 3a) and may be explained by the different porosities and pore sizes. The pore size evolutions for the three kinds of fabrics with increasing PPy loading are shown in Fig. 4. For the knitted fabric, the average pore diameter was reduced from 45 to 10 μm when the PPy loading was increased from 0 to 7.96 mg cm$^{-2}$ (Fig. 4a). For the woven fabric, the average pore diameter decreased from 11 to 1.8 μm with increasing the PPy loading from 0 to 5.88 mg cm$^{-2}$ (Fig. 4b). For the nonwoven fabric, this diameter was reduced from 50 to 14 μm when the PPy loading increased from 0 to 4.33 mg cm$^{-2}$ (Fig. 4c). Therefore, for the woven fabric, the pore size is too small to facilitate further pyrrole infiltration and subsequent polymerization will occur in the solution instead of on the fibers. As for the nonwoven fabric, the pore size is too large, resulting in a lack of polymerization sites. Consequently, the thick PPy layer is likely to be peeled off from the fiber upon washing with water. For the knitted fabric, optimal porosity and pore size brings about a high loading capacity.

Fig. S12† compares cyclic voltammograms of the supercapacitors based on the three kinds of PPy-coated fabrics. The curves share the same shape but have different areas, which indicates similar redox reactions but different specific capacitances. The redox properties of PPy are related to the anion expulsion/incorporation process as detailed in the following equation:$^{37}$

$$\text{PPy} + A^- \xrightarrow{\text{oxidise}} \text{PPy}^+ A^- + e^-$$
A represents the available anions, which are $\text{SO}_4^{2-}$ and AQSA$^-$ ions in the present situation. Therefore, there are two corresponding stages in the CV spectrum in both the oxidization and reduction processes as shown in Fig. S12.† The knitted structure displayed the highest electrochemical performance and was carefully investigated further. For the PPy-coated knitted fabric with a loading density of 12.3 mg cm$^{-2}$, the galvanostatic charge/discharge curves were reproducible (Fig. 5a). The areal specific capacitances were 4117, 3553, 2956, 2516 and 2212 mF cm$^{-2}$ at 2, 5, 10, 15 and 20 mA cm$^{-2}$, respectively (Fig. 5b). The fabric supercapacitors were stable for up to 5000 cycles (Fig. 5c). The loading capability of the knitted fabric may exceed the highest values previously reported for porous substrates; therefore the resulting supercapacitor showed the highest area specific capacitance amongst the supercapacitors in this work (Fig. 5d). Note that the pore configuration of the knitted fabric also facilitates charge transport under charging and discharging.

The supercapacitor based on two PPy-coated knitted fabrics was also investigated for its flexibility and stability. Importantly, the specific capacitances remained almost unchanged under bending, with the bending angle increased to 180° for 500 cycles (Fig. 6a). The specific capacitances were also well maintained under twisting, with the twisting angle increased to 90° for 500 cycles (Fig. 6b). Good flexibility and stability were also achieved by the supercapacitors based on both the PPy-coated

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**Fig. 5** Electrochemical properties of PPy-coated knitted fabrics with a PPy mass loading of 12.3 mg cm$^{-2}$. (a) Voltage profiles during galvanostatic charging and discharging. (b) Rate performance. (c) Long-life performance. (d) Comparison with the other supercapacitors which incorporate conducting polymers through the use of porous frameworks. The data are extracted from Table S1.†

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**Fig. 6** Flexibility of the supercapacitor assembled from the same two PPy-coated knitted fabrics under (a) bending and (b) twisting. The PPy mass loading was 12.3 mg cm$^{-2}$. 

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woven and nonwoven fabrics (Fig. S13†). The energy density increased from 3.19 to 5.94 W h kg⁻¹ when the power density decreased from 259.55 to 25.97 W kg⁻¹ with respect to the total mass of the two electrodes (Fig. S14†). When compared with previous works, the proposed supercapacitor has an advantage due to the energy density (Fig. S14†).

Conclusions

In conclusion, the porosity and pore configuration of the fabrics were controlled by the fabric construction, and have a great effect on the loading capability of the active material and the subsequent electrochemical properties. The optimal fabric with a porosity of 80% and an average pore size of 45 μm produced a high PPy mass loading of 12.3 mg cm⁻², which exceeds previous supercapacitors and lithium-ion batteries. In addition, a record high areal specific capacitance of 4117 mF cm⁻² was achieved. These novel supercapacitor fabrics are flexible and exhibit stable performances under various deformations such as bending and twisting, which offers them promising applications in many emerging fields, such as portable and wearable electronics. This work also presents a new, general and effective strategy towards the development of the next-generation of energy storage devices.

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