High-performance cotton fabric-based supercapacitors consisting of polypyrrole/Ag/graphene oxide nanocomposite prepared via UV-induced polymerization

Chunliu Liang · Limin Zang · Fangfang Shi · Chao Yang · Jianhui Qiu · Qifan Liu · Zhenming Chen

Abstract Cotton fabric (CF) fabricated by natural cellulose fibers has porous structure, abundant hydrophilic hydroxyl groups and good mechanical flexibility, which is a promising substrate for flexible fabric-based supercapacitors. Graphene oxide (GO) nanosheets were fixed on the CF by vacuum filtration, and then the pyrrole monomers and silver ions (Ag⁺) were adsorbed to the surface of GO/CF by π-π and electrostatic interactions, respectively. Polypyrrole/silver (PPy/Ag) nanoparticles were generated on the surface of GO/CF via in situ UV-induced polymerization, forming the flexible PPy/Ag/GO/CF electrodes. The electrodes combine three active materials (PPy, Ag and GO), which show good electrochemical performance. The electrode prepared under optimum conditions (UV irradiation time: 120 min; mass loading of GO on the CF: 3 mg cm⁻²) exhibits a high specific capacitance of 1664.0 mF cm⁻². The flexible symmetric quasi-solid-state fabric-based supercapacitor (QFSC) based on the optimum electrode also keeps superior electrochemical performance and excellent mechanical flexibility, which has a great application prospect for wearable energy storage devices.

Keywords Polypyrrole · Silver nanoparticles · Cotton fabric · Flexible supercapacitor · UV-induced polymerization

Introduction

With the rapid development of wearable technology, various wearable electronic products emerge in an endless stream, which in turn makes flexible energy storage devices become a research hotspot (Dubal et al. 2018; Sumboja et al. 2018; Yu et al. 2019). Among several popular flexible energy storage devices (flexible supercapacitors, flexible lithium-ion batteries, flexible zinc-ion batteries, etc.), flexible
supercapacitors are particularly noticeable due to their environmental friendliness, fast charge/discharge rate, high power density, long cycle life and superior mechanical flexibility (Dai et al. 2021; Jia et al. 2020; Keum et al. 2020; Xiong et al. 2021; Zhang et al. 2021). Especially, flexible fabric-based supercapacitors are regarded as the suitable energy storage device for wearable electronic devices because they are easy to integrate into cloths. In addition, the 3D porous structure and excellent mechanical flexibility of the fabrics are conducive to loading more active materials on the fabrics and improving the electrochemical and mechanical performance of the fabric-based supercapacitors. Compared with the synthetic fabrics consisting of man-made fibers, cotton fabric (CF) fabricated by natural cellulose fibers has good hydrophilicity, breathability and renewability, which is a promising candidate for flexible fabric-based supercapacitors. To fabricate flexible supercapacitors, graphene is often applied as the active material on account of its large specific surface area, good electrical conductivity, high mechanical robustness and outstanding cycling stability. However, the poor hydrophilicity, strong van der Waals forces and π–π interactions of graphene can have negative effects on its electrochemical performance. After oxidation, the obtained graphene oxide (GO) shows improved hydrophilicity and the abundant oxygen-containing functional groups of GO can have strong interaction with the hydroxyl groups of CF, which are advantageous to obtaining the flexible fabric-based supercapacitor with good electrochemical and mechanical performance by loading GO on the CF (GO/CF). Even so, limited by the electric double layer capacitance (EDLC) mechanism of GO, the specific capacitance of GO/CF needs to be further improved by introducing other active materials.

Polypyrrole (PPy), as a representative conducting polymer, is one of the most concerned pseudocapacitive materials for flexible supercapacitors in light of its good environmental stability, outstanding electrochemical properties, easy preparation, high conductivity and low cost. The composite electrodes containing pseudocapacitive PPy and electric double layer capacitive GO possess improved electrochemical performance due to the synergistic effect. To obtain PPy, UV-induced polymerization of pyrrole in the presence of silver ions (Ag+) has been proven to be a simple and effective method. This strategy can not only obtain PPy nanoparticles in a relatively short time, but also generate Ag nanoparticles simultaneously. The incorporation of Ag nanoparticles can improve the electrical conductivity and store energy via reversible redox reaction, which can further enhance the electrochemical performance of the electrode materials.

In this study, GO nanosheets were anchored on the CF by vacuum filtration to obtain the flexible GO/CF. Pyrrole monomers and Ag+ ions were gathered on the surface of GO/CF due to the π-π interaction between GO and pyrrole monomers and electrostatic interaction between GO and Ag+ ions. Then PPy/Ag nanoparticles were generated on the GO/CF via in situ UV-induced polymerization, forming the flexible PPy/Ag/GO/CF electrodes. The as-prepared PPy/Ag/GO/CF electrodes show superior electrochemical performance owing to the synergistic effect of the three active materials (PPy, Ag and GO). In addition, the strong interactions among components and high mechanical flexibility of CF endow the PPy/Ag/GO/CF electrodes with outstanding mechanical flexibility and robustness. The effects of each component, UV irradiation time and mass loading of GO on the CF on the electrochemical properties were studied. The PPy/Ag/GO/CF electrode with the best electrochemical performance was further used to fabricate a flexible symmetric supercapacitor, exhibiting excellent mechanical flexibility and electrochemical performance.

Experimental section

Materials

Graphite, sulfuric acid (H₂SO₄, 98%), nitric acid (HNO₃, 68%), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), hydrogen peroxide (H₂O₂, 30%), ethanol, pyrrole, silver nitrate (AgNO₃), ammonium persulfate (APS) and poly(vinyl alcohol) (PVA).
were analytically pure and bought from Aladdin Co. Ltd.

Fabrication of graphene oxide/cotton fabric (GO/CF)

CF (5 × 5 cm²) was cut from old T-shirts and washed with ethanol to remove impurities before use. GO was synthesized according to the modified Hummers method (Tian et al. 2019), and then was dispersed in distilled water to obtain a GO suspension (2 mg mL⁻¹). GO/CF was prepared by vacuum filtration and then dried at 80 °C for 12 h. The as-prepared GO/CF with 1, 2, 3 and 4 mg of GO on one square centimeter of CF are labeled as 1GO/CF, 2GO/CF, 3GO/CF and 4GO/CF, respectively.

Fabrication of flexible PPy/Ag/GO/CF electrodes

The PPy/Ag/GO/CF electrodes were prepared by UV-induced polymerization. Typically, 0.25 mL of pyrrole was stirred in 25 mL of distilled water for 30 min in an ice-water bath, and then 10 mL of AgNO₃ solution (containing 0.612 g of AgNO₃) was added with stirring for 5 min. Then the mixture and GO/CF were transferred to a petri dish to perform the UV-induced polymerization (wavelength of the UV light: 365 nm). After UV irradiation for a certain time, the samples were washed with distilled water and ethanol, and dried at 40 °C in a vacuum oven for 12 h to obtain the PPy/Ag/GO/CF electrodes. The final PPy/Ag/GO/CF electrodes are named as PPy/Ag/xGO/CFₙ, where x is the mass loading of GO on one square centimeter of CF (1, 2, 3 and 4 mg cm⁻²) and n means the UV irradiation time (60, 90, 120 and 150 min).

For comparison, traditional chemical polymerization of pyrrole was also performed to prepare the fabric-based electrode. In brief, 0.25 mL of pyrrole and 0.33 g of HNO₃ were stirred in 25 mL of distilled water for 30 min in an ice-water bath, and then 3GO/CF was added into the mixture. Afterwards, 10 mL of APS solution (containing 0.83 g of APS) was slowly added into the mixture within 20 min, and the mixture was stirred for 8 h in an ice-water bath to obtain the PPy/3GO/CF electrode.

Assembly of flexible quasi-solid-state fabric-based supercapacitor (QFSC)

Firstly, PVA/H₂SO₄ gel electrolyte was prepared by dissolving 6 g of PVA in 60 mL of 1 M H₂SO₄ solution at 85 °C and then cooled to room temperature. Two pieces of PPy/Ag₃GO/CF₁₂₀ electrodes were immersed in the PVA/H₂SO₄ electrolyte for 5 min and dried for 60 min at room temperature. The QFSC with a sandwich structure was assembled by pressing the above electrodes together (effective area: 1 × 1 cm²).

Characterization

The morphology and structure of the samples were characterized by field emission scanning electron microscope (SEM, ZEISS Sigma 300), Raman spectroscopy (Thermo Scientific DXR), X-ray diffractometer (XRD, PANalytical X’Pert Pro) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi). The electrochemical properties of the electrodes and QFSC were tested by CS2350H electrochemical workstation (Wuhan Corrtest Instruments Co. Ltd.). The electrochemical calculations are given in the Supporting Information.

Results and discussion

Figure 1 schematically illustrates the fabrication process of the flexible PPy/Ag/GO/CF electrodes by UV-induced polymerization. The CF obtained from old T-shirts is woven by natural cellulose fibers, showing a porous microstructure (Fig. S1a). After vacuum filtration of GO suspension, GO nanosheets are coated on the CF (Fig. S1b) and have strong interactions with CF owing to the hydrogen bonds formed between oxygen-containing functional groups of GO and hydroxyl groups of CF. As confirmed in Fig. S2, no GO nanosheets fall off the CF even after ultrasonic treatment for 120 min. When GO/CF is submerged in the aqueous solution containing pyrrole and AgNO₃, the pyrrole monomers are gathered on the surface of GO/CF due to π-π interaction between pyrrole and GO. Meanwhile, Ag⁺ ions are also adsorbed onto the surface of GO/CF due to electrostatic interaction between Ag⁺ and GO. The formation mechanism of PPy/Ag composite by UV-induced polymerization is
shown in Fig. S3 (Zang et al. 2016). Pyrrole monomers are excited and undergo polymerization to form PPy when exposed to UV light, and Ag$^+$ ions are reduced to the metallic Ag nanoparticles at the same time, leading to the formation of flexible PPy/Ag/GO/CF electrodes.

Raman spectra of 3GO/CF and PPy/Ag/3GO/CF$_{120}$ are displayed in Fig. 2a. For 3GO/CF, two marked peaks at 1346 cm$^{-1}$ (D band) attributed to the defects and/or edges of carbon atom lattice and 1592 cm$^{-1}$ (G band) assigned to the in-plane stretching vibration of sp$^2$ hybridized carbon appear (Han et al. 2018). For PPy/Ag/3GO/CF$_{120}$, the main peaks of PPy are confirmed, including ring in-plane deformation associated with radical cation at 974 cm$^{-1}$, symmetrical C–H in-plane bending at 1041 cm$^{-1}$, C–C in-ring stretching at 1340 cm$^{-1}$ and C=C stretching of the PPy backbone at 1581 cm$^{-1}$ (Lv et al. 2019b; Zuo et al. 2020). Additionally, the D band and G band of GO are shifted and overlapped with the peaks of PPy, which is resulted from π–π interaction between PPy and GO (Singu and Yoon 2018). Figure 2b shows the XRD patterns of 3GO/CF and PPy/Ag/3GO/CF$_{120}$. The strong diffraction peak of 3GO/CF at 2θ = 10.6°...
is ascribed to the (001) diffraction of GO. The interlayer distance between graphene layers of the GO is 0.86 nm according to Bragg’s equation, which is wider than that of the corresponding graphite due to the presence of oxygen-containing functional groups (Fan et al. 2017; Saleem et al. 2018). For the XRD pattern of PPy/Ag/3GO/CF_{120}, five peaks loaded at 38.0°, 44.2°, 64.3°, 77.3° and 81.5° are corresponded to the (111), (200), (220), (311) and (222) planes of Ag with face-centered cubic structure (JCPDS 87-0597) (Cai et al. 2017). It is indicated that Ag^+ ions have been reduced to metallic Ag nanoparticles during UV-induced polymerization process. Moreover, the diffraction peak of GO decreases because the 3GO/CF is covered by PPy/Ag nanoparticles.

To further confirm the chemical state of the PPy/Ag/GO/CF electrodes, 3GO/CF and PPy/Ag/3GO/CF_{120} are analyzed by XPS spectra. As shown in Fig. 3a, the XPS survey spectrum of 3GO/CF has two prominent peaks referring C1s and O1s, and PPy/Ag/3GO/CF_{120} shows four major peaks referring to C1s, O1s, N1s and Ag3d, indicating the formation of PPy and Ag via UV-induced polymerization. Figure 3b reveals the high-resolution XPS spectrum of C1s in the PPy/Ag/3GO/CF_{120}, in which the prominent peaks of C−C (284.0 eV), C−N (285.3 eV), =C−NH+ (286.6 eV) and −C=N+ (288.4 eV) can be distinguished (Singu and Yoon 2018). More significantly, the high-resolution XPS spectrum of N1s shown in Fig. 3c can be divided into four peaks, including −N= (397.2 eV), −NH− (399.2 eV), −N− (400.8 eV) and NO_{3−} (405.7 eV) (Cao et al. 2015). The existence of protonated benzenoid amine nitrogen demonstrates that the PPy has been doped. The high-resolution XPS spectrum of Ag3d shown in Fig. 3d has two peaks of Ag3d_{5/2} (367.7 eV) and Ag3d_{3/2} (373.7 eV), proving the presence of Ag nanoparticles (Zhou et al. 2020).

The effects of UV irradiation time on the morphology and electrochemical properties of the electrodes are studied. Figure 4 shows the SEM images of PPy/Ag/1GO/CF_y electrodes with different UV irradiation time. PPy/Ag/1GO/CF_{60} possesses plenty of holes because the PPy/Ag nanoparticles generated within 60 min are limited and cannot completely cover the surface of GO/CF. As the UV irradiation time extends, the generated PPy/Ag nanoparticles become more and more, and the surface morphology of PPy/Ag/1GO/CF_y electrode gets denser and denser. Specifically, the produced PPy/Ag nanoparticles on the 1GO/CF in 60, 90, 120 and 150 min are 0.9, 2.9, 3.5 and 3.9 mg cm^{-2}, respectively. The electrochemical
properties of PPy/Ag/1GO/CF\textsubscript{y} electrodes are investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS). As shown in Fig. 5a, the CV curves of PPy/Ag/1GO/CF\textsubscript{y} electrodes have a pair of redox peaks situated in ~0.56 V and ~0.48 V, which are associated with faradic reactions of Ag/Ag\textsuperscript{+} (Li et al. 2018; Wei et al. 2013). GCD curves of PPy/Ag/1GO/CF\textsubscript{y} electrodes (Fig. 5b) exhibit voltage platforms, which correspond to the CV curves. PPy/Ag/1GO/CF\textsubscript{120} electrode exhibits the largest CV curve area and longest discharge time, suggesting it has the highest specific capacitance. By calculation, the areal specific capacitance (\(C_A, \text{ electrode}\)) and volumetric specific capacitance (\(C_V, \text{ electrode}\)) of the PPy/Ag/1GO/CF\textsubscript{y} electrodes at different current densities are shown in Fig. S4. Among them, the PPy/Ag/1GO/CF\textsubscript{120} electrode has the highest \(C_A, \text{ electrode}\) of 690.3 mF cm\textsuperscript{-2} and \(C_V, \text{ electrode}\) of 11.4 F cm\textsuperscript{-3} at a current density of 0.5 mA cm\textsuperscript{-2}. When the current density increases to 5 mA cm\textsuperscript{-2}, the PPy/Ag/1GO/CF\textsubscript{120} electrode still shows the highest \(C_A, \text{ electrode}\) of

![Fig. 4 SEM images of (a) PPy/Ag/1GO/CF\textsubscript{60}, (b) PPy/Ag/1GO/CF\textsubscript{90}, (c) PPy/Ag/1GO/CF\textsubscript{120} and (d) PPy/Ag/1GO/CF\textsubscript{150}](image)

![Fig. 5 Electrochemical properties of PPy/Ag/1GO/CF\textsubscript{y} electrodes. (a) CV curves at 1 mV s\textsuperscript{-1}; (b) GCD curves at 0.5 mA cm\textsuperscript{-2}; (c) Nyquist plots](image)
237.9 mF cm$^{-2}$ and $C_{V, \text{electrode}}$ of 3.9 cm$^{-3}$, but the capacitance retention is only 34.5%. The result demonstrates that 120 min is the optimum UV irradiation time for the preparation of PPy/Ag/GO/CF electrode with high specific capacitance. Although the produced PPy/Ag nanoparticles in 150 min are more than that in 120 min, the dense and compact structure of PPy/Ag/1GO/CF$_{150}$ will cause that less active sites can be exposed and the diffusion of electrolyte ions becomes more difficult. Nyquist plots of the PPy/Ag/1GO/CF$_{y}$ electrodes shown in Fig. 5c are divided into two regions, including the semicircle at the high-frequency region and the straight line at the low-frequency region. The PPy/Ag/1GO/CF$_{120}$ electrode possesses the lowest charge transfer resistance ($R_{ct}$) of 12.4 $\Omega$, indicating that it has easy charge transfer at the electrode/electrolyte interface.

With more profound research, it is found that the mass loading of GO on the CF significantly affects the morphology and electrochemical properties of the electrodes. Figure 6 shows the SEM images of PPy/Ag/GO/CF$_{120}$ electrodes with different mass loading of GO on the CF. The produced PPy/Ag nanoparticles gradually increase and then decrease as the mass loading of GO on the CF increases. To be specific, the produced PPy/Ag nanoparticles on the 1GO/CF, 2GO/CF, 3GO/CF and 4GO/CF in 120 min are 3.5, 4.3, 6.3 and 5.1 mg cm$^{-2}$, respectively. The produced PPy/Ag nanoparticles in PPy/Ag/3GO/CF$_{120}$ reach the maximum value of 6.3 mg cm$^{-2}$, and the Ag, C, N and O elements are uniformly distributed (Fig. 6e–h). The GO has abundant oxygen-containing functional groups on its surface. The higher mass loading of GO on the CF means that more active sites are exposed, so more Ag$^{+}$ ions and pyrrole monomers are adsorbed on the surface of GO/CF to realize the high yield of PPy/Ag nanoparticles. But when the mass loading of GO on the CF is superabundant (4 mg cm$^{-2}$ in this work), agglomeration happens due to the strong interactions between GO nanosheets, which leads to the
appearance of cracks and the reduction of active sites. As a result, the produced PPy/Ag nanoparticles in PPy/Ag/4GO/CF<sub>120</sub> (5.1 mg cm<sup>-2</sup>) is lower than that of PPy/Ag/3GO/CF<sub>120</sub>.

The electrochemical properties of PPy/Ag/1GO/CF<sub>120</sub>, PPy/Ag/2GO/CF<sub>120</sub>, PPy/Ag/3GO/CF<sub>120</sub> and PPy/Ag/4GO/CF<sub>120</sub> electrodes are shown in Fig. 7. PPy/Ag/3GO/CF<sub>120</sub> electrode exhibits the maximum value of CV curve area (Fig. 7a) and discharge time (Fig. 7b), indicating it has the best specific capacitance. The rate performance of PPy/Ag/xGO/CF<sub>120</sub> electrodes is shown in Fig. S5. The C<sub>A, electrode</sub> of PPy/Ag/3GO/CF<sub>120</sub> electrode at a current density of 0.5 mA cm<sup>-2</sup> is 1664.0 mF cm<sup>-2</sup> (C<sub>V, electrode</sub>: 27.0 F cm<sup>-3</sup>) and reaches 780.7 mF cm<sup>-2</sup> when the current density is 5 mA cm<sup>-2</sup> (C<sub>V, electrode</sub>: 12.7 F cm<sup>-3</sup>), with a capacitance retention of 46.9%. The high specific capacitance of PPy/Ag/3GO/CF<sub>120</sub> electrode is attributed to the highest content of PPy/Ag nanoparticles. In addition, PPy/Ag/3GO/CF<sub>120</sub> electrode has the smallest equivalent series resistance (R<sub>s</sub>, 3.7 Ω) and R<sub>ct</sub> (1.9 Ω) according to the Nyquist plots shown in Fig. 7c, which is also conducive to the electrochemical performance. The CV curves of 1GO/CF, 2GO/CF, 3GO/CF and 4GO/CF shown in Fig. S6a present nearly rectangle shapes and the corresponding GCD curves shown in Fig. S6b display nearly symmetrical triangles, demonstrating the EDLC behavior of GO (Yang et al. 2020). Compared with PPy/Ag/GO/CF electrodes, the specific capacitance of GO/CF is very limited. The maximum C<sub>A, electrode</sub> of GO/CF is only 14.4 F cm<sup>-2</sup> at a current density of 0.5 mA cm<sup>-2</sup>, which indicates that PPy/Ag nanoparticles have a major contribution to the capacitance. To better illustrate the effect of Ag nanoparticles, the electrochemical properties of PPy/3GO/CF electrode and PPy/Ag/3GO/CF<sub>120</sub> electrode are compared in Fig. S7. The CV curve of PPy/3GO/CF electrode is an approximately rectangular shape (Fig. S7a) and the GCD curve is an approximately symmetrical triangle (Fig. S7b), revealing its typical capacitive behavior (Zang et al. 2020). Significantly different from PPy/3GO/CF electrode, the CV curve of PPy/Ag/3GO/CF<sub>120</sub> electrode shows much larger enclosed area and the corresponding GCD curve has much longer discharge time than those of PPy/3GO/CF electrode. The values of C<sub>A, electrode</sub> and C<sub>V, electrode</sub> of PPy/3GO/CF electrode are only 393.7 mF cm<sup>-2</sup> and 6.5 F cm<sup>-3</sup> at a current density of 0.5 mA cm<sup>-2</sup>, respectively (Fig. S7c). The pair of strong peaks in the CV curve and the voltage platforms in the GCD curve are attributed to the reversible Ag/Ag<sup>+</sup> redox, indicating that the Ag nanoparticles can store/release charges and contribute to the capacitance (Li et al. 2018; Wei et al. 2013). Moreover, the presence of Ag nanoparticles in the electrode can increase the electrical conductivity and improve the ability of charge transfer. According to the Nyquist plots shown in Fig. S7d, the R<sub>s</sub> and R<sub>ct</sub> of PPy/3GO/CF electrode are 8.2 Ω and 20.2 Ω, respectively, which are higher than those of PPy/Ag/3GO/CF<sub>120</sub> electrode.

To sum up, there are four reasons can be explained the excellent electrochemical performance of PPy/Ag/3GO/CF<sub>120</sub> electrode. (i) The 3GO/CF can provide more active sites to effectively adsorb more pyrrole monomers and Ag<sup>+</sup> ions on its surface to form more PPy/Ag nanoparticles. (ii) To perform the UV-induced polymerization for 120 min can achieve the high yield of PPy/Ag nanoparticles with appropriate compactness, which is

![Fig. 7 Electrochemical properties of PPy/Ag/xGO/CF<sub>120</sub> electrodes. a CV curves at 1 mV s<sup>-1</sup>; b GCD curves at 0.5 mA cm<sup>-2</sup>; c Nyquist plots](image)
beneficial to provide more active substances, expose more active sites and achieve fast ion diffusion. (iii) The Ag nanoparticles not only can effectively increase the electrical conductivity and improve the ability of charge transfer, but also can contribute to the capacitance through the reversible Ag/Ag⁺ redox. (iv) The synergistic effect of the three active materials (PPy, Ag and GO) is advantageous to improve the electrochemical performance of the electrode. Moreover, PPy/Ag/3GO/CF₁₂₀ electrode shows outstanding mechanical flexibility owing to the strong interactions among components and the high mechanical flexibility of CF. As shown in Fig. S8, the tensile strength of PPy/Ag/3GO/CF₁₂₀ electrode is 5.42 MPa with a break elongation of 6.34%, which is even a little higher than that of CF (tensile strength: 5.26 MPa, break elongation: 5.84%). Two pieces of PPy/Ag/3GO/CF₁₂₀ electrode are further used to prepare the flexible QFSC (Fig. 8a). The CV curves of the QFSC show a pair of redox peaks at low scan rates, and the peaks gradually shift and become weak and wide with the increase of scan rate (Fig. 8b). To better understand the charge storage mechanism of the QFSC, the relationship between the total measured voltammetry charge ($q_v$) and inverse of the square root of the scan rate ($v^{-1/2}$) is plotted in Fig. 8c. According to the electrochemical calculations given in the Supporting Information (Ardizzone et al. 1990), the outer surface charges ($q_o$) of the QFSC which is a non-diffusion controlled process, is calculated to be $0.05377$ C cm⁻² by linear fitting. The $q_v$ of the QFSC at 1, 2, 4, 5, 10 and 20 mV s⁻¹ are 0.19, 0.16, 0.14, 0.13, 0.10 and 0.07 C cm⁻², respectively. The corresponding ratios of non-diffusion contribution at different scan rates are shown in Fig. 8d, which increases from 28.5% at 1 mV s⁻¹ to 77.9% at 20 mV s⁻¹ because the electrolyte ions don’t have enough time to diffuse into and diffuse out of the inner part of the active materials at high scan rates. The GCD curves with good symmetry demonstrate that the QFSC has superior electrochemical reversibility and high Coulombic efficiency (Fig. 8e). Fig. S9 shows the areal specific capacitance ($C_{A,\text{device}}$) and volumetric specific capacitance ($C_{V,\text{device}}$) of the QFSC at 0.5, 1, 2, 4 and 5 mA cm⁻². The maximum $C_{A,\text{device}}$ and $C_{V,\text{device}}$ can reach 286.6 mF cm⁻² and 4.7 F cm⁻³ at 0.5 mA cm⁻², respectively, and $C_{A,\text{device}}$ and $C_{V,\text{device}}$ still can reach 187.2 mF cm⁻² and 3.0 F cm⁻³ at 5 mA cm⁻², respectively.

![Fig. 8](https://example.com/fig8.png)

**Fig. 8** Electrochemical properties of the QFSC based on the PPy/Ag/3GO/CF₁₂₀ electrode. a Structure schematic illustration; b CV curves at different scan rates; c The dependence of $q_v$ on $v^{-1/2}$; d The ratios of non-diffusion contribution at different scan rates; e GCD curves at various current densities; f Nyquist plots.
revealing its high specific capacitance and excellent rate performance. And the values of $R_s$ and $R_{ct}$ obtained from the Nyquist plot in Fig. 8f are 5.3 Ω and 2.4 Ω, respectively.

The Ragone plots of the QFSC are shown in Fig. 9a. The maximum energy density is 25.5 μWh cm$^{-2}$ at a power density of 101.6 μW cm$^{-2}$, and the maximum power density is 1149.5 μW cm$^{-2}$ at an energy density of 16.6 μWh cm$^{-2}$. It is superior compared with other reported similar supercapacitors, such as rGO/PPy (Barakzehi et al. 2019), graphene/nanotube/PANI (Liu et al. 2020b), PPy CNT/cotton yarn plywood (Hao et al. 2021), PPy/graphite/newspaper (Zang et al. 2020), PANI/PPy/graphite/gold-coated sandpaper (Alcaraz-Espinoza and de Oliveira 2018), and PPy/gold-coated surgical mask (Zuo et al. 2022). Also, the capacitance retention of the QFSC is 90.5% after 10,000 GCD cycles (Fig. 9b). The good cycling stability may be attributed to two reasons: (1) No active materials peel off during GCD cycling process due to the strong interactions among components; (2) The flexible substrate (CF) can ease the structural breakdown of PPy caused by repetitive insertion and de-insertion of counter ions. In addition, the QFSC exhibits outstanding flexibility. As shown in Fig. 9c, the CV curves are negligibly changed at different bending curvatures of 60°, 120° and 180° compared with its normal state. Surprisingly, after 10,000 bending cycles at a bending angle of 180°, the capacitance retention is still as high as 89.7%, which is ascribed to that the 3GO/CF can provide robust and flexible support for PPy/Ag nanoparticles to maintain the electrode integrity. At the same time, the working voltage and capacitance can be adjusted by connecting multiple QFSCs in series and in parallel to meet the practical requirements. Figure 9e shows the GCD curves of multiple QFSCs connected in series and in parallel. The voltage window can extend to 2.4 V by connecting three QFSCs in series, and the discharge time increases three folds while the working voltage is unchanged by connecting three QFSCs in parallel. For example, as shown in Fig. 9f, three QFSCs connected in series can power the electronic clock effortlessly, indicating the as-prepared QFSC is a good candidate for wearable electronics.

![Fig. 9 Electrochemical performance of the QFSC based on the PPy/Ag/3GO/CF$_{120}$ electrode. a Ragone plots; b Cycling stability at 8 mA cm$^{-2}$; c CV curves at 10 mV s$^{-1}$ under different bending angles; d Capacitance retention during 10,000 bending cycles at a bending angle of 180°; e GCD curves of QFSCs connected in series and in parallel; f Digital image of an electronic clock powered by three QFSCs connected in series]
Conclusion

In summary, the flexible PPy/Ag/GO/CF electrodes can be conveniently obtained by efficient UV-induced polymerization. The incorporation of Ag nanoparticles can effectively enhance the electrical conductivity and contribute to the capacitance through the reversible Ag/Ag⁺ redox. The optimum UV irradiation time and the mass loading of GO on the CF are determined to be 120 min and 3 mg cm⁻², respectively. The corresponding PPy/Ag/3GO/CF₁₂₀ electrode exhibits a high specific capacitance of 1664.0 mF cm⁻² (27.0 F cm⁻³) owing to the high yield of PPy/Ag nanoparticles with appropriate compactness and the synergistic effect of PPy, Ag and GO. The as-assembled QFSC based on the PPy/Ag/3GO/CF₁₂₀ electrode possesses maximum specific capacitance of 286.6 mF cm⁻² (4.7 F cm⁻³), energy density of 25.5 μWh cm⁻² and power density of 1149.5 μW cm⁻². In addition, the device retains 89.7% of its original capacitance after 10,000 bending cycles, exhibiting its excellent mechanical flexibility and electrochemical stability. In light of the outstanding electrochemical performance and feasible preparation process, this study offers an effective method to obtain flexible and wearable energy storage device with high performance.

Acknowledgments We acknowledge support from the National Natural Science Foundation of China (No. 51763008), the Natural Science Foundation of Guangxi Province (Nos. 2019GXNSFAA245028, 2018GXNSFAA281241), and the Opening Project of Guangxi Key Laboratory of Calcium Carbonate Resources Comprehensive Utilization (HZXYKFKT201909).

Funding The authors have not disclosed any funding.

Conflict of interest The authors have not disclosed any competing interests.

References

Alcaraz-Espinoza JJ, de Oliveira HP (2018) Flexible supercapacitors based on a ternary composite of polyaniline/polypyrrole/graphite on gold coated sandpaper. Electrochim Acta 274:200–207. https://doi.org/10.1016/j.electacta.2018.04.063

Ardizzone S, Fregonara G, Trasatti S (1990) Inner and outer active surface of RuO₂ electrodes. Electrochim Acta 35:263–267. https://doi.org/10.1016/0013-4686(90)85068-x

Barakzhei M, Montazer M, Sharif F, Norby T, Chatzitakis A (2019) A textile-based wearable supercapacitor using reduced graphene oxide/polypyrrole composite. Electrochim Acta 305:87–196. https://doi.org/10.1016/j.electacta.2019.03.058

Cai Y, Wu D, Zhu X, Wang W, Tan F, Chen J, Qiao X, Qiu X (2017) Sol-gel preparation of Ag-doped MgO nanoparticles with high efficiency for bacterial inactivation. Ceram Int 43:1066–1072. https://doi.org/10.1016/j.ceramint.2016.10.041

Cao J, Wang Y, Chen J, Li X, Walsh FC, Ouyang JH, Jia D, Zhou Y (2015) Three-dimensional graphene oxide/polypyrrole composite electrodes fabricated by one-step electrosorption for high performance supercapacitors. J Mater Chem A 3:14445–14457. https://doi.org/10.1039/C5TA02920A

Dai L, Wang Y, Li W, Zhao W, Duan C, Xiong C, Ni Y (2021) A green all-polysaccharide hydrogel platform for sensing and electricity harvesting/storage. J Power Sources 493:229711. https://doi.org/10.1016/j.jpowsour.2021.229711

Dubal DP, Chodankar NR, Kim DH, Gomez-Romero P (2018) Towards flexible solid-state supercapacitors for smart and wearable electronics. Chem Soc Rev 47:2065–2129. https://doi.org/10.1039/C7CS00505A

Fan Z, Zhu J, Sun X, Cheng Z, Liu Y, Wang Y (2017) High density of free-standing holey graphene/PPy films for superior volumetric capacitance of supercapacitors. ACS Appl Mater Interfaces 9:21763–21772. https://doi.org/10.1021/acsami.7b03477

Han Y, Zhang Z, Yang M, Li T, Wang Y, Cao A, Chen Z (2018) Facile preparation of reduced graphene oxide/polypyrrole nanocomposites with urchin-like microstructure for wide-potential-window supercapacitors. Electrochim Acta 289:238–247. https://doi.org/10.1016/j.electacta.2018.09.040

Hao B, Deng Z, Bi S, Ran J, Cheng D, Luo L, Cai G, Wang X, Tang X (2021) In situ polymerization of pyrrole on CNT/cotton multifunctional composite yarn for supercapacitors. Ionics 27:279–288. https://doi.org/10.1007/s11581-020-03784-2

Huang L, Santiago D, Loyselle P, Dai L (2018) Graphene-based nanomaterials for flexible and wearable supercapacitors. Small 14:1800879. https://doi.org/10.1002/smll.201800879

Jia R, Shen G, Qu F, Chen D (2020) Flexible on-chip microsupercapacitors: efficient power units for wearable electronics. Energy Storage Mater 27:169–186. https://doi.org/10.1016/j.ensm.2020.01.030

Keum K, Kim JW, Hong SY, Son JG, Lee SS, Ha JS (2020) Flexible/stretchable supercapacitors with novel functionality for wearable electronics. Adv Mater 32:2002180. https://doi.org/10.1002/adma.202002180

Kim YK, Shin KY (2021) Dopamine-assisted chemical vapour deposition of polypyrrole on graphene for flexible supercapacitor. Appl Surf Sci 547:149141. https://doi.org/10.1016/j.apsusc.2021.149141
Li J, Sun Y, Wang J, Tian J, Zhang X, Yang H, Lin B (2018) Synthesis, structure and electrochemical properties of novel ternary composite reduced-graphene oxide/Ag nanoparticles/poly(p-phenylenediamine). J Alloys Compd 749:783–793. https://doi.org/10.1016/j.jallcom.2018.03.326

Li Z, Tian M, Sun X, Zhao H, Zhu S, Zhang X (2019) Flexible all-solid planar fibrous cellulose nonwoven fabric-based supercapacitor via capillarity-assisted graphene/MnO2 assembly. J Alloys Compd 782:986–994. https://doi.org/10.1016/j.jallcom.2018.12.254

Li Z, Li M, Fan Q, Qi X, Qu L, Tian MW (2021) Smart-fabric-based supercapacitor with long-term durability and waterproof properties toward wearable applications. ACS Appl Mater Interfaces 13:14778–14785. https://doi.org/10.1021/acsami.1c02615

Liang C, Yang C, Zang L, Liu Q, Qiu J, Li Y, Zuo W, Liu X (2021) UV-assisted one-step synthesis of ternary graphene/polypyrrole/silver nanocomposites for supercapacitors. Energy Technol 9:200966. https://doi.org/10.1002/ente.20200966

Liu Q, Zang L, Qiao X, Qiu J, Wang X, Hu L, Yang J, Yang C (2019) Compressible all-in-one supercapacitor with adjustable output voltage based on polypyrrole-coated melamine foam. Adv Electron Mater 5:1900724. https://doi.org/10.1002/aelm.201900724

Liu K, Yao Y, Lv T, Li H, Li N, Chen Z, Qian G, Chen T (2020a) Textile-like electrodes of seamless graphene/nanotubes for wearable and stretchable supercapacitors. J Power Sources 446:227355. https://doi.org/10.1016/j.jpowsour.2019.227355

Liu Q, Qiu J, Yang C, Zang L, Zhang G, Sakai E (2020b) High-performance textile electrode enhanced by surface modifications of fiberglass cloth with polypyrrole tentacles for flexible supercapacitors. Int J Energy Res 44:9166–9176. https://doi.org/10.1002/er.5558

Lv J, Zhang L, Zhong Y, Sui X, Wang B, Chen Z, Feng X, Xu H, Mao Z (2019a) High-performance polypyrrole coated knitted cotton fabric electrodes for wearable energy storage. Org Electron 74:59–68. https://doi.org/10.1016/j.orgel.2019.06.027

Lv J, Zhou P, Zhang L, Zhong Y, Sui X, Wang B, Chen Z, Xu H, Mao Z (2019b) High-performance polypyrrole textile electrodes for wearable electronics obtained by an improved in situ polymerization method. Chem Eng J 361:897–907. https://doi.org/10.1016/j.cej.2018.12.083

Purkait T, Singh G, Kumar D, Singh M, Ramendra Sundar Dey RS (2018) High-performance flexible supercapacitors based on electrochemically tailored three-dimensional reduced graphene oxide networks. Sci Rep 8:1–13. https://doi.org/10.1038/s41598-018-18593-3

Saleem H, Haneef M, Abbasi HY (2018) Synthesis route of reduced graphene oxide via thermal reduction of chemically exfoliated graphene oxide. Mater Chem Phys 204:1–7. https://doi.org/10.1016/j.matchemphys.2017.10.020

Singu BS, Yoon KR (2018) Highly exfoliated GO-PPy-Ag ternary nanocomposite for electrochemical supercapacitor. Electrochim Acta 268:304–315. https://doi.org/10.1016/j.electacta.2018.02.076

Sumboja A, Liu J, Zheng WG, Zong Y, Zhang H, Liu Z (2018) Electrochemical energy storage devices for wearable technology: a rationale for materials selection and cell design. Chem Soc Rev 47:5919–5945. https://doi.org/10.1039/C8CS00237A

Tian J, Wu S, Yin X, Wu W (2019) Novel preparation of hydrophilic graphene/graphene oxide nanosheets for supercapacitor electrode. Appl Surf Sci 496:143696. https://doi.org/10.1016/j.apsusc.2019.143696

Wang N, Han G, Xiao Y, Li Y, Song H, Zhang Y (2018a) Polypyrrole/graphene oxide deposited on two metalized surfaces of porous polypropylene films as all-in-one flexible supercapacitors. Electrochim Acta 270:490–500. https://doi.org/10.1016/j.electacta.2018.03.090

Wang Y, Zhang Y, Zhang W, Qiu J, Liu Q, Peng W, Liu X, Li M, Wang D (2018b) Flexible supercapacitor with high energy density prepared by GO-induced porous coral-like polypyrrole (PPy)/PET non-woven fabrics. J Mater Sci 53:8409–8419. https://doi.org/10.1007/s10853-018-2131-9

Wang N, Wang X, Zhang Y, Hou W, Chang Y, Song H, Zhao Y, Han G (2020a) All-in-one flexible asymmetric supercapacitor based on composite of polypyrrole-graphene oxide and poly(3,4-ethylenedioxythiophene). J Alloys Compd 835:155299. https://doi.org/10.1016/j.jallcom.2020.155299

Wang W, Sadak O, Guan J, Gunasekaran S (2020b) Facile synthesis of graphene paper/polypyrrole nanocomposite as electrode for flexible solid-state supercapacitor. J Energy Storage 30:101533. https://doi.org/10.1016/j.est.2020.101533

Wang B, Li Z, Yin Y, Wang C (2021) Center and multi-points current collecting for improving capacitances of rectangular polypyrrole/knitted cotton fabric-based supercapacitor. J Power Sources 481:228824. https://doi.org/10.1016/j.jpowsour.2020.228824

Wei J, Xing G, Gao L, Suo H, He X, Zhao C, Li S, Xing S (2013) Nickel foam based polypyrrole–Ag composite film: a new route toward stable electrodes for supercapacitors. New J Chem 37:337–341. https://doi.org/10.1039/C2NJ40590C

Wu DY, Shao JJ (2021) Graphene-based flexible all-solid-state supercapacitors. Mater Chem Front 5:557–583. https://doi.org/10.1039/d0qm00291g

Xiong C, Li B, Duan C, Dai L, Nie S, Qin C, Xu Y, Ni Y (2021) Carbonized wood cell chamber-reduced graphene oxide@PVA flexible conductive material for supercapacitor, strain sensing and moisture-electric generation applications. Chem Eng J 418:129518. https://doi.org/10.1016/j.cej.2021.129518

Yang C, Hu L, Zang L, Liu Q, Qiu J, Yang J, Qiao X (2020) High-performance all-solid-state supercapacitor based on activated carbon coated fiberglass cloth using asphalt as active binder. J Electrochem Soc 167:020540. https://doi.org/10.1149/1945-7111/ab6bb

Yu P, Zeng Y, Zhang H, Yu M, Tong Y, Lu X (2019) Flexible Zn-ion batteries: recent progresses and challenges. Small 15:1804760. https://doi.org/10.1002/smll.201804760

Zang L, Qiu J, Yang C, Sakai E (2016) Preparation and application of conducting polymer/Ag/clay composite nanoparticles formed by in situ UV-induced dispersion polymerization. Sci Rep 6:20470. https://doi.org/10.1038/srep24070
Zang L, Qiao X, Liu Q, Yang C, Hu L, Yang J, Ma Z (2020) High-performance solid-state supercapacitors with designable patterns based on used newspaper. Cellulose 27:1033–1042. https://doi.org/10.1007/s10570-019-02856-5

Zhang X, Wang J, Liu J, Wu J, Chen H, Bi H (2017) Design and preparation of a ternary composite of graphene oxide/carbon dots/polypyrrole for supercapacitor application: Importance and unique role of carbon dots. Carbon 115:134–146. https://doi.org/10.1016/j.carbon.2017.01.005

Zhang C, Tian J, Rao W, Guo B, Fan L, Xu W, Xu J (2019) Polypyrrole@metal-organic framework (UIO-66)@cotton fabric electrodes for flexible supercapacitors. Cellulose 26:3387–3399. https://doi.org/10.1007/s10570-019-02321-3

Zhang X, Jiang C, Liang J, Wu W (2021) Electrode materials and device architecture strategies for flexible supercapacitors in wearable energy storage. J Mater Chem A 9:8099–8128. https://doi.org/10.1039/D0TA12299H

Zhou C, Wang Q, Yan XH, Wang JJ, Wang DF, Yuan XX, Jiang H, Zhu YH, Cheng XN (2020) A facile route to synthesize Ag decorated MoO3 nanocomposite for symmetric supercapacitor. Ceram Int 46:15385–15391. https://doi.org/10.1016/j.ceramint.2020.03.083

Zuo W, Zang L, Wang X, Liu Q, Qiu J, Liang C, Liu X, Yang C (2020) Flexible polypyrrole@Fe3O4@stainless steel yarn composite electrode for symmetric thread-like supercapacitor with extended operating voltage window in Li2SO4-based aqueous electrolyte. Adv Sustain Syst 4:2000173. https://doi.org/10.1002/adss.202000173

Zuo W, Zang L, Liu Q, Qiu J, Lan M, Yang C (2022) A quasi-solid-state supercapacitor based on waste surgical masks with high flexibility and designable shape. Colloid Surf A 634:128020. https://doi.org/10.1016/j.colsurfa.2021.128020

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.