High-Performance Cotton Fabric-Based Supercapacitors Consisting of Polypyrrole/Ag/Graphene Oxide Nanocomposite Prepared Via UV-Induced Polymerization

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Research Article

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

Posted Date: October 27th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1009537/v1>

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Version of Record: A version of this preprint was published at Cellulose on February 3rd, 2022. See the published version at <https://doi.org/10.1007/s10570-022-04454-4>.

Abstract

Cotton fabric (CF) fabricated by natural cellulose fibers has porous structure and abundant hydrophilic hydroxyl groups, 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 in situ generated on the surface of GO/CF via UV-induced polymerization, forming the flexible PPy/Ag/GO/CF electrodes. The electrodes combine three active materials (PPy, Ag and GO) 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 $1664.0 \text{ mF cm}^{-2}$). 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 is expected to have great application prospect for wearable energy storage devices.

1. 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 (Jia et al. 2020; Keum et al. 2020; 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 (Barakzahi et al. 2019; Li et al. 2021; Liu et al. 2020a). 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 (Li et al. 2019; Lv et al. 2019a; Wang et al. 2021; Zhang et al. 2019).

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 (Huang et al. 2018; Purkait et al. 2018; Wu and Shao 2021). 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 introduction of 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 (Kim and Shin 2021; Liu et al. 2019; Wang et al. 2020a; Zang et al. 2020). The composite electrodes containing pseudocapacitive PPy and electric double layer capacitive GO possess improved electrochemical performance due to the synergistic effect (Wang et al. 2018a; Wang et al. 2020b; Wang et al. 2018b; Zhang et al. 2017). 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 (Liang et al. 2021; Zang et al. 2016). 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 (Li et al. 2018; Liang et al. 2021), which can further enhance the electrochemical performance of the electrode materials.

Thus, in this study, GO nanosheets were anchored on the CF by vacuum filtration to obtain the flexible GO/CF firstly, and then PPy/Ag nanoparticles were in situ formed on the GO/CF to achieve the flexible PPy/Ag/GO/CF electrodes via UV-induced polymerization. The strong interactions among components and high mechanical flexibility of the CF endow the PPy/Ag/GO/CF electrodes with outstanding mechanical flexibility and robustness. Moreover, the PPy/Ag/GO/CF electrodes show superior electrochemical performance owing to the combination of PPy, Ag and GO. The effects of UV irradiation time as well as the 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 which also exhibits excellent mechanical flexibility and electrochemical performance.

2. Experimental Section

2.1 Materials

Graphite, sulfuric acid (H_2SO_4 , 98%), nitric acid (HNO_3 , 68%), potassium permanganate (KMnO_4), sodium nitrate (NaNO_3), hydrogen peroxide (H_2O_2 , 30%), ethanol, pyrrole, silver nitrate (AgNO_3), ammonium persulfate (APS) and poly(vinyl alcohol) (PVA) were analytically pure and bought from Aladdin Co. Ltd.

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

CF ($5 \times 5 \text{ cm}^2$) 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.

2.3 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 for 12 h to obtain the PPy/Ag/GO/CF electrodes. The final PPy/Ag/GO/CF electrodes are named as PPy/Ag/xGO/CF_y, where x is the mass loading of GO on one square centimeter of CF (1, 2, 3 and 4 mg cm⁻²) and y 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.

2.4 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).

2.5 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.

3. 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, which has hydroxyl groups and porous microstructure (Fig. S1a). After vacuum filtration of GO suspension, GO nanosheets are coated on the CF (Fig. S1b) and has 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 AgNO_3 , 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 exposure 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/CF₁₂₀ 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 in-plane stretching vibration of sp^2 hybridized carbon appear (Han et al. 2018). For PPy/Ag/3GO/CF₁₂₀, 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, 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). Fig. 2b shows the XRD patterns of 3GO/CF and PPy/Ag/3GO/CF₁₂₀. The strong diffraction peak of 3GO/CF at $2\theta = 10.6^\circ$ is ascribed to the (001) diffraction of GO. The interlayer distance between graphene layers of the GO is 0.86 nm according to the 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/CF₁₂₀, 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/CF₁₂₀ 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/CF₁₂₀ shows four major peaks referring to C1s, O1s, N1s and Ag3d, indicating the formation of PPy and Ag via UV-induced polymerization. Fig. 3b reveals the high-resolution XPS spectrum of C1s in the PPy/Ag/3GO/CF₁₂₀, in which the prominent peaks of C-C (284.0 eV), C-N (285.3 eV), $=\text{C}-\text{NH}^+$ (286.6 eV) and $-\text{C}=\text{N}^+$ (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 $-\text{N}=$ (397.2 eV), $-\text{NH}-$ (399.2 eV), $-\text{N}^+-$ (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 $\text{Ag}3\text{d}_{5/2}$ (367.7 eV) and $\text{Ag}3\text{d}_{3/2}$ (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. Fig. 4 shows the SEM images of PPy/Ag/1GO/CF_y electrodes with different UV irradiation time. PPy/Ag/1GO/CF₆₀ possesses plenty of holes because the PPy/Ag nanoparticles generated within 60 min are limited and cannot completely cover the surface of GO/CF. With 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_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_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⁺ (Li et al. 2018; Wei et al. 2013). GCD curves of PPy/Ag/1GO/CF_y electrodes (Fig. 5b) exhibit voltage platforms, which correspond to the CV curves. The PPy/Ag/1GO/CF₁₂₀ electrode exhibits the largest CV curve area and longest discharge time, suggesting it has the highest specific capacitance. By calculation, the areal specific capacitance ($C_{A, electrode}$) and volumetric specific capacitance ($C_{V, electrode}$) of the PPy/Ag/1GO/CF_y electrodes at different current densities are shown in Fig. S4. Among them, the PPy/Ag/1GO/CF₁₂₀ electrode has the highest $C_{A, electrode}$ of 690.3 mF cm⁻² and $C_{V, electrode}$ of 11.4 F cm⁻³ at a current density of 0.5 mA cm⁻². When the current density increases to 5 mA cm⁻², the PPy/Ag/1GO/CF₁₂₀ electrode still shows the highest $C_{A, electrode}$ of 237.9 mF cm⁻² and $C_{V, electrode}$ of 3.9 cm⁻³. The result demonstrates that 120 min is the optimum UV irradiation time for preparation of PPy/Ag/GO/CF electrode with high specific capacitance. Although the produced PPy/Ag nanoparticles in 150 min is more than that in 120 min, the dense and compact structure of PPy/Ag/1GO/CF₁₅₀ 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/CF₁₂₀ electrode possesses the lowest charge transfer resistance (R_{ct}) of 12.4 Ω, 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. Fig. 6 shows the SEM images of PPy/Ag/xGO/CF₁₂₀ 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. The produced PPy/Ag nanoparticles in PPy/Ag/3GO/CF₁₂₀ reach the maximum value of 6.3 mg cm⁻², and the Ag, C, N and O elements are uniformly distributed (Fig. 6e-h). However, when the mass loading of GO on the CF is 4 mg cm⁻², the surface of PPy/Ag/4GO/CF₁₂₀ shows various degrees of cracks. 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/CF₁₂₀ (5.1 mg cm^{-2}) is lower than that of PPy/Ag/3GO/CF₁₂₀.

The electrochemical properties of PPy/Ag/1GO/CF₁₂₀, PPy/Ag/2GO/CF₁₂₀, PPy/Ag/3GO/CF₁₂₀ and PPy/Ag/4GO/CF₁₂₀ electrodes are shown in Fig. 7. The PPy/Ag/3GO/CF₁₂₀ electrode exhibits the maximum value of CV curve area (Fig. 7a) and discharge time (Fig. 7b), indicating it has the best specific capacitance. As shown in Fig. S5, the $C_{A, electrode}$ of PPy/Ag/3GO/CF₁₂₀ electrode at a current density of 0.5 mA cm^{-2} is $1664.0 \text{ mF cm}^{-2}$ ($C_{V, electrode}$: 27.0 F cm^{-3}) and reaches 780.7 mF cm^{-2} when the current density is 5 mA cm^{-2} ($C_{V, electrode}$: 12.7 F cm^{-3}). The high specific capacitance and good rate performance of PPy/Ag/3GO/CF₁₂₀ electrode is attributed to the highest content of PPy/Ag nanoparticles. In addition, the PPy/Ag/3GO/CF₁₂₀ electrode has the smallest equivalent series resistance (R_s , 3.7Ω) and R_{ct} (1.9Ω) 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 $C_{A, electrode}$ of GO/CF is only 14.4 F cm^{-2} a current density of 0.5 mA cm^{-2} , which indicates that the PPy/Ag nanoparticles have 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/CF₁₂₀ electrode are compared in Fig. S7. The CV curve of the PPy/3GO/CF electrode is an approximately rectangular shape (Fig. S7a) and the GCD curve is approximately symmetrical triangle (Fig. S7b), revealing its typical capacitive behavior (Zang et al. 2020). Significantly different from the PPy/3GO/CF electrode, the CV curve of PPy/Ag/3GO/CF₁₂₀ electrode shows much larger enclosed area and the corresponding GCD curve has much longer discharge time than those of the PPy/3GO/CF electrode. The values of $C_{A, electrode}$ and $C_{V, electrode}$ of the PPy/3GO/CF electrode are only 393.7 mF cm^{-2} and 6.5 F cm^{-3} at a current density of 0.5 mA cm^{-2} , 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⁺ redox, which indicate 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 charge transfer ability. According to the Nyquist plots shown in Fig. S7d, the R_s and R_{ct} of the PPy/3GO/CF electrode are 8.2Ω and 20.2Ω , respectively, which are higher than those of the PPy/Ag/3GO/CF₁₂₀ electrode.

To sum up, there are four reasons can be explained the excellent electrochemical performance of the PPy/Ag/3GO/CF₁₂₀ electrode. (⊗) The 3GO/CF can provide more active sites to effectively adsorb more pyrrole monomers and Ag⁺ ions on its surface to form more PPy/Ag nanoparticles. (⊗) To perform the UV-induced polymerization for 120 min can achieve the high yield of PPy/Ag nanoparticles with appropriate

compactness, which is beneficial to expose more active sites and achieve fast ion diffusion. (X) The Ag nanoparticles not only can effectively increase the electrical conductivity and improve the charge transfer ability of the electrode, but also can contribute to the capacitance through the reversible Ag/Ag⁺ redox. (X) The synergistic effect of the three active materials (PPy, Ag and GO) is advantageous to improve the electrochemical performance of the electrode. 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 $\sim 0.054 \text{ C cm}^{-2}$ 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. S8 shows the areal specific capacitance ($C_{A, device}$) and volumetric specific capacitance ($C_{V, device}$) of the QFSC at 0.5, 1, 2, 4 and 5 mA cm^{-2} , which reveals its high specific capacitance and excellent rate performance. The maximum $C_{A, device}$ and $C_{V, device}$ can reach 286.6 mF cm^{-2} and 4.7 F cm^{-3} at 0.5 mA cm^{-2} , respectively. 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 $\mu\text{Wh cm}^{-2}$ at a power density of 101.6 $\mu\text{W cm}^{-2}$, and the maximum power density is 1149.5 $\mu\text{W cm}^{-2}$ at an energy density of 16.6 $\mu\text{Wh cm}^{-2}$. It is superior compared with other reported similar flexible supercapacitors, such as rGO/PPy (Barakzahi et al. 2019), Graphene/nanotube/PANI (Liu et al. 2020b), rGO/1, 4, 5, 8 tetrahydroxy anthraquinone (Xu et al. 2017), PPy CNT/cotton yarn plywood (Hao et al. 2021), PPy-PVA hydrogel (Zang et al. 2017), and graphene film (Li et al. 2017). Also, the capacitance retention of the QFSC is 90.5% after 10000 GCD cycles (Fig. 9b), demonstrating its good cycling stability. 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 10000 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. Fig. 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.

4. Conclusion

In summary, the flexible PPy/Ag/GO/CF electrodes can be conveniently obtained by efficient in situ UV-induced polymerization on the surface of GO/CF. 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 10000 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 high-performance.

Declarations

ACKNOWLEDGMENT

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

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Figures

Figure 1

Schematic fabrication process of the flexible PPy/Ag/GO/CF electrodes

Figure 2

a Raman spectra and b XRD patterns of 3GO/CF and PPy/Ag/3GO/CF₁₂₀

Figure 3

a XPS survey spectra of 3GO/CF and PPy/Ag/3GO/CF₁₂₀ and corresponding XPS spectra of b C1s, c N1s and d Ag3d in the PPy/Ag/3GO/CF₁₂₀

Figure 4

SEM images of a PPy/Ag/1GO/CF60, b PPy/Ag/1GO/CF90, c PPy/Ag/1GO/CF120 and d PPy/Ag/1GO/CF150

Figure 5

Electrochemical properties of PPy/Ag/1GO/CFy electrodes. a CV curves at 1 mV s⁻¹; b GCD curves at 0.5 mA cm⁻²; c Nyquist plots

Figure 6

SEM images of a PPy/Ag/1GO/CF120, b PPy/Ag/2GO/CF120, c PPy/Ag/3GO/CF120 and d PPy/Ag/4GO/CF120; EDS mappings of e Ag, f C, g N and h O of PPy/Ag/3GO/CF120

Figure 7

Electrochemical properties of PPy/Ag/xGO/CF120 electrodes. a CV curves at 1 mV s⁻¹; b GCD curves at 0.5 mA cm⁻²; c Nyquist plots

Figure 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

Figure 9

Electrochemical performance of the QFSC based on the PPy/Ag/3GO/CF120 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 10000 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.

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