

Research Papers

Application of long fibrous coconut silk-based porous carbon in flexible supercapacitor

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ABSTRACT

All-solid-state flexible supercapacitors are considered to be one of the ideal candidates for energy storage in the next generation of wearable electronic devices due to their high capacitance performance and excellent mechanical flexibility. Biomass-based carbon materials are regarded as the ideal precursors for carbon-based electrode materials due to their wide sources, low cost, natural and abundant biological features. In this work, long-fiber coconut silk with vascular bundle structure was selected as the precursor, the controllable adjustment of the pore structure and conductive characteristics of the electrode material was achieved by changing the KOH activation temperature. The specific surface area of the activated carbon electrode material etched with KOH at 900 °C can reach 2794 m²·g⁻¹. The high specific surface area and reasonable pore size distribution provide abundant active sites for the adsorption of electrolyte ions, which leads to the excellent electrode specific capacitance (2 mV·s⁻¹, 634 F·g⁻¹, 10.73 Wh·kg⁻¹) of the symmetric flexible supercapacitor combined with PVA (polyvinyl alcohol)/H₂SO₄ gel electrolyte. At the same time, the long-fiber carbon skeleton has intrinsically high Young's modulus, which enables the flexible all-solid-state supercapacitor to maintain better electrochemical stability and mechanical durability under mechanical deformation, and its retention rate can reach 101.5 % after 10,000 bending experiments at an inner angle of 140°. It proves the great advantages and potential of coconut silk-based biomass carbon materials in the field of preparing flexible supercapacitors, and promotes the development of energy storage units for next-generation wearable electronic devices.

1. Introduction

With the development of the concept of Internet of Things (IoT) and artificial intelligence technology, wearable sensing and monitoring electronic devices are gradually becoming popular [1]. In addition to the development of functional materials and device structures, the energy storage problem of wearable devices has also received extensive attention [2,3]. Compared with traditional rigid lithium batteries, supercapacitors are regarded as the best choice for the next generation of new energy storage methods due to their high capacity, fast charge and discharge rate, wide operating temperature range and excellent cycle stability [4,5]. Pseudocapacitive supercapacitors dominated by metal oxides usually exhibit high specific capacitance and energy density, but the structure of electrode materials is easy to be gradually destroyed with the occurrence of chemical reactions, thus resulting in poor cycle

stability [6,7]. At the same time, the rigid electrode material makes the device often exhibit poor mechanical flexibility, which also makes the device at risk of leakage under continuous mechanical deformation [8,9]. The main electrode materials of double-layer supercapacitors are carbon-based materials such as activated carbon, carbon nanotubes and graphene [10–12]. Carbon based materials usually show excellent capacitance performance and good cycle stability due to their excellent conductivity, large specific surface area and abundant hierarchical pore structure. Moreover, carbon-based materials have abundant frame structures and generally exhibit higher mechanical endurance [13]. The flexible all-solid-state supercapacitor combined with gel electrolyte has good capacitive performance and excellent mechanical flexibility, so it is regarded as an effective solution to replace the traditional rigid battery in wearable electronic devices [14].

The sources of carbon materials are very rich, among which biomass

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carbon materials are widely distributed in nature and the price is low [15–18]. They have formed a natural spatial structure and high carbon content during hundreds of million years of evolution, which make the biomass materials ideal precursors for the fabrication of carbon-based electrodes for supercapacitors [19–22]. Biomass materials such as eggs [23], wool textiles [24], areca palm leaves [25], soybean sprouts [26], rapeseed cake [27], and chitin [28], etc. can be processed through a simple carbonization and activation method to obtain porous, highly graphitized carbon materials, which are widely used in the preparation of flexible supercapacitors. However, these materials still suffer from structural collapse during the carbonization and activation process, resulting in a reduction in specific surface area and poor electrical conductivity, which in turn show poor capacitor output performance [9,29–31]. The specific surface area (SBET), pore volume (V_{tot}), and electrode resistance (R_s) are the three most important factors affecting the capacitance performance of supercapacitors, which have been fully verified in our previous machine learning research work [9,32]. Therefore, the preparation of carbon electrodes with high specific surface area, reasonable pore structure and low conduction resistance has become an urgent problem to be solved in the process of preparing flexible supercapacitors. Long-fiber plants such as taro stems [33], weedy wood fibers [34], wheat straw [35], cotton stalks [36], etc. are internally composed of vessels and sieve tubes, usually showing tubular or vascular bundle-like side-by-side hollow structures. At the same time, many natural pores are distributed on the tube wall, which have the characteristics of intrinsic high specific surface area [9]. This connected hollow structure enables the activator to fully penetrate into the material during the activation process to improve the activation rate, which is beneficial to the formation of rich hierarchical pore structure and high electrical conductivity, and the densely packed carbon skeleton can maintain the stability of the overall structure in the process of carbonization and activation [37]. Therefore, long fiber plant-based derived carbon material is expected to become an ideal electrode material for flexible all-solid-state supercapacitors.

Coconut silk, a typical long fibrous plant with vascular bundles, is an ideal precursor for carbon electrodes. In this work, coconut silk was used as carbon source, and the pore structure and conductive properties of long fiber carbon materials were effectively regulated by adjusting the activation temperature of KOH, and the structure-activity relationship between these factors and capacitive properties was explored. It is found that the electrode material with a reasonable proportion of hierarchical pore distribution can exhibit optimal electrolyte diffusion and adsorption capacity, which in turn leads to excellent capacitive performance. In addition, the porous carbon electrode prepared by this method was combined with PVA/ H_2SO_4 gel electrolyte to prepare an all-solid-state flexible supercapacitor to explore the application prospect of this carbon-based porous electrode material in the field of flexible energy storage. With the help of the natural mechanical strength of the biomass carbon framework and the flexibility of the gel electrolyte, the composite device not only exhibits excellent capacitance performance, but also exhibits good mechanical stability and durability, which provides good guidance for the design of next-generation high-performance flexible energy storage devices.

2. Experimental

2.1. Synthesis of carbon materials

The coconut silks were purchased from Hainan province, China. The acetylene black and polytetrafluoroethylene binder were purchased from Aiweixin Chemical Technology (Tianjin) Co. LTD. The H_2SO_4 was purchased from Fuyu Fine Chemical (Tianjin) Co. LTD. The KOH was purchased from Damao Chemical Reagent Factory (Tianjin). The PVA (1799, Viscosity: 25–31 mPa·s, alcoholysis degree: 98–99 % (mol/mol), molecular weight: 72000–77,000) was purchased from Aladdin Reagent (Shanghai) Co. LTD. All chemicals in the present work were analytical

reagent grades and were used as received without further purifications (Fig. 1).

The coconut silk fibers were washed several times with distilled water, dried sufficiently, and placed in a CVD tube furnace under continuous Ar flow atmosphere for pre-carbonization. The carbonization process was to stand at 400 °C for 1 h, and the heating and cooling rates were both 5 °C per minute. The obtained product was cleaned with deionized water, and the black precarbonized carbon material was obtained after drying at 50 °C for 12 h.

The pre-carbonized powder samples were mixed with KOH at a mass ratio of 1:4, and then placed in a tube furnace with a continuous Ar flow atmosphere for activation at 800 °C, 900 °C, and 1000 °C, respectively, and which the activation time was 1 h. After the reaction, the cooled sample was fully washed with deionized water until it reaches neutrality (pH = 7) in order to remove impurities (unreacted KOH and byproducts such as K) generated from the reaction. After cleaning, they were dried at 50 °C for 12 h to obtain carbon electrode materials with different activation conditions, which were marked as CF-800, CF-900, and CF-1000, respectively.

2.2. Preparation of the electrodes and all-solid-state flexible supercapacitors

Mixed the activated carbon material with acetylene black and polytetrafluoroethylene binder in a mass ratio of 8:1:1, the precursor paste can be formed by adding an appropriate amount of ethanol and continuously agitation. Took an appropriate amount of paste and press it with a tablet machine, a uniform disk like electrode sheet with a diameter of 0.8 cm and the thickness of 300 μm was formed after dried at 110 °C for 4 h. Two electrodes with similar quality were respectively placed on the surface of hydrophilic carbon paper, separated from each other by polypropylene film, and 1 M H_2SO_4 was used as the electrolyte. Then, a traditional symmetrical supercapacitor is assembled in the order of stainless steel shell, gasket, electrode group, gasket, and shell.

The preparation method of electrode materials for all-solid-state flexible supercapacitors is similar to that of traditional capacitors, except that the electrolyte used PVA/ H_2SO_4 gel as the solid electrolyte. The preparation method was to mix 1.0 g PVA with 7 mL deionized water, and the PVA gel was obtained after continuously stirred at 80 °C until clarified. Then, 3 mL of 3.4 M H_2SO_4 solution was added to the prepared PVA gel, and the mixture was keep stirring at 60 °C for 30 min to obtain a transparent PVA/ H_2SO_4 gel electrolyte. After that, the two electrodes and septum (polypropylene film, thickness: 25 μm , poriness: 41–55 %) with similar mass were respectively soaked in PVA/ H_2SO_4 gel electrolyte at 60 °C for 4 h, and carbon cloth was used as the current collector. The electrodes and septum were then assembled in a sandwich structure in turn, and finally encapsulated with polyimide PI tape to obtain an all-solid-state flexible supercapacitor.

2.3. Characterizations

The surface morphologies and microstructures of the carbon electrodes were investigated by Scanning Electron Microscope (SEM, SU3500, Hitachi). The X-ray diffraction (XRD, Bruker, Cu-K α , λ = 1.57418 Å) and Raman spectra (RTS-2, Titan Electro-Optics (Hong Kong) Co. Ltd., 532 nm) were used to analyze the composition and structure of the synthetic materials. The decomposition temperature of the biomass carbon material was characterized by thermogravimetric analysis experiments (Mettler Toledo TG2). The BET specific surface area was analyzed by N_2 adsorption isotherms with ASAP 2460 (Micromeritics) instrument at 77 K. The electrical conductivity of different carbon electrodes was characterized by a four-probe station (C-4, EVERBEING) with source meter (Keithley 2612B).

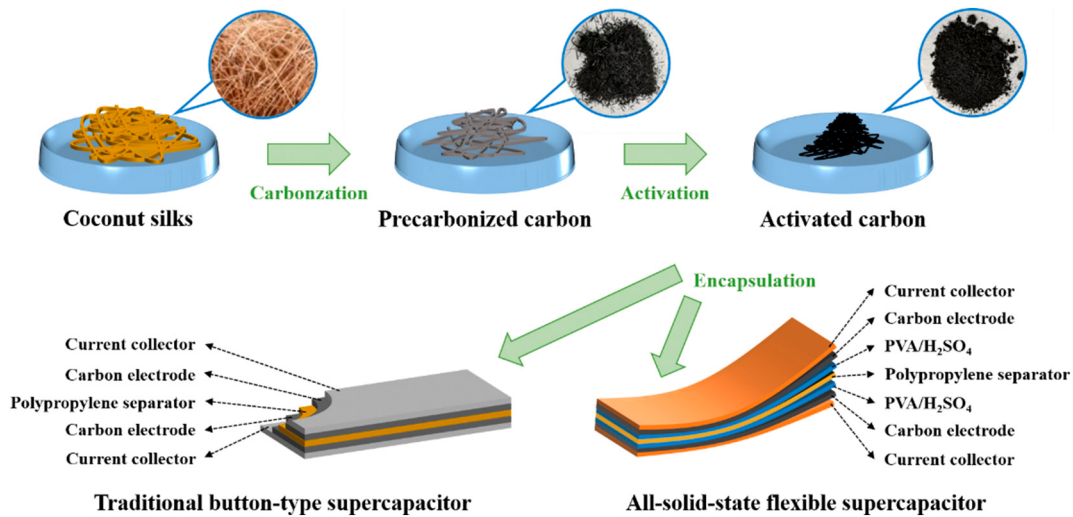


Fig. 1. Schematic illustration of the synthesis process for coconut silk-based supercapacitor.

2.4. Electrochemical measurements

The prepared electrode materials, electrolytes and separators were assembled into symmetrical button-type conventional supercapacitors and all-solid-state flexible supercapacitors for electrochemical tests and analysis. The cyclic voltammetry curve (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) of the device were tested by electrochemical workstation (CHI 760E). 1 M H_2SO_4 and PVA/ H_2SO_4 gel were used as electrochemical test electrolytes for conventional supercapacitors and all-solid-state flexible supercapacitors, respectively. The CV and GCD tests were both conducted by the two-electrode method, the test range is 0–0.8 V. The EIS measurements were conducted in the frequency ranging from 0.01 to 100 kHz with an AC voltage (5 mV). The mechanical stability of all-solid-state flexible supercapacitors was measured by a self-made extensometer and electrochemical workstation.

According to the CV curves, the specific capacitance of supercapacitor can be calculated from the following equation:

$$C_{mD} = \frac{1}{2} \frac{\int I(V)dV}{v \Delta V} \quad (1)$$

where C_{mD} ($\text{F} \cdot \text{g}^{-1}$) is the device specific capacitance, I ($\text{A} \cdot \text{g}^{-1}$) is the current density, V (V) is the applied voltage, $\int I(V)dV$ is the mathematical integral area of CV curve, ΔV (V) and v ($\text{mV} \cdot \text{s}^{-1}$) refer to the operating voltage window and scan rate respectively.

According to the charge/discharge curves, the specific capacitance of supercapacitor can be calculated from the following equation:

$$C_{mD} = \frac{I_d \Delta t}{\Delta V m} \quad (2)$$

where C_{mD} ($\text{F} \cdot \text{g}^{-1}$) is the device specific capacitance, I_d (A) is the discharge current, Δt (s) is the discharge time, ΔV (V) and m (g) refer to the discharge voltage range and mass loading of active materials respectively. The energy density (E , $\text{Wh} \cdot \text{kg}^{-1}$) and power density (P , $\text{W} \cdot \text{kg}^{-1}$) can be calculated by C_{mD} from the following equation:

$$E = \frac{1}{2} C_{mD} \Delta V^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

The electrode specific capacitance (C_{mE}) and device specific capacitance (C_{mD}) satisfy the relationship of $C_{mE} = 4 \cdot C_{mD}$, which the multiplier of 4 adjusts the capacitance of the device and the combined mass of

two electrodes to the capacitance and mass of a single electrode. The specific capacitance described in this paper is the electrode specific capacitance.

3. Results and discussion

Before the experiment, the thermal stability of each component in coconut silk was analyzed by thermogravimetric test to find the appropriate pre-carbonization temperature. The specific test results and analysis process are shown in Fig. S1. Based on the results of thermogravimetric analysis, 400 °C was selected as the pre-carbonization temperature in this experiment, which not only ensures the complete decomposition of lignin, but also facilitates the graphitization of carbon materials, which was conducive to the preparation of carbon precursors with excellent electrical conductivity [38].

Fig. 2A and B show the intrinsic morphology of coconut silk, and it can be seen that there are abundant vascular bundles and hollow tubes in the material, which are mainly sieve tubes responsible for transporting water and nutrients in the long fiber biomass material. The diameter of a single tube is about 5–10 μm , and flute-like pores are evenly distributed inside the tube wall. The interconnecting hollow structure provides a natural porous template for the subsequent carbonization and activation process of the material. Fig. 2C shows the morphology of the material after the pre-carbonization operation. It can be seen that the activated material still maintains the porous vascular bundle structure of the original biomass material, which indicates that the carbonization operation only removes the biological components such as lignin in the material without destroying itself. At the same time, the pre-carbonization operation can expose the pore structure of the biomass, and the cavities are connected to each other to form a hollow skeleton structure, which is conducive to the embedding of the activator in the subsequent activation process, thereby improving the activation efficiency.

Fig. 2D–F show the morphologies of the samples after activation with KOH as the activator at different temperatures, respectively, and table S1 illustrates the evolution of chemical reactions during the activation process. It can be seen that the carbon wall of the sample becomes thinner after the activation treatment, and the whole sample presents an irregular porous honeycomb structure. The lamellae support each other, which effectively hinders the mutual stacking and agglomeration of carbon materials [39]. By comparing Fig. 2E and D, it can be seen that with the increase of activation temperature, the activation process of the material is more sufficient, which makes the micropores on the carbon skeleton increase to the size of mesopores. The micropores with smaller

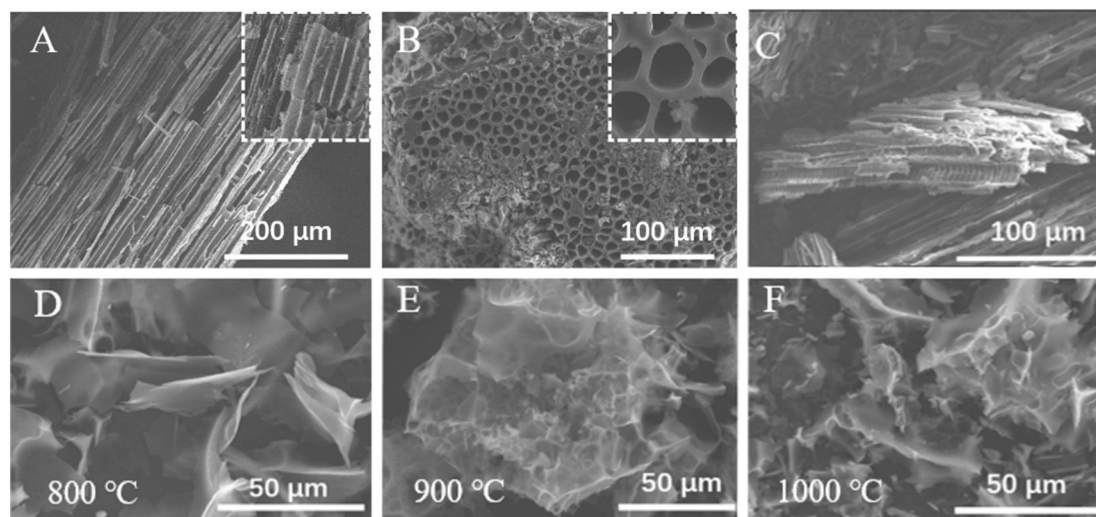


Fig. 2. Front and cross section SEM images of (A, B) original coconut silks with different magnification, (C) Pre-carbonized material, (D) CF-800, (E) CF-900, (F) CF-1000.

sizes are distributed on the pore walls, presenting a hierarchical porous structure. Further increase the activation temperature, the etching effect of KOH on the carbon skeleton is enhanced. Excessive etching causes the original carbon skeleton to collapse and further damage the structure [40]. Part of the damaged carbon sheets or particles will fill the pore structure and reduce the specific surface area of the material. At the same time, it will hinder the contact between activated carbon material and electrolyte, thus weakening the conduction of electrolyte ions. Therefore, the activated carbon material prepared by activation at 900 °C can maintain a complete hierarchical porous structure, which is beneficial to the sufficient contact between the electrolyte and the carbon material, which in turn is beneficial to achieve excellent capacitive performance.

The crystal structures of the samples prepared under different conditions were characterized by XRD, and the results are shown in Fig. 3A. It can be seen that all three samples have relatively obvious diffraction peaks at 22° and 43°, corresponding to the (002) and (100) crystal planes of carbon, respectively [41]. These diffraction results collectively describe the order degree information between graphitic interlayer and graphitic layer in carbon-based materials. First, the broad diffraction peak at 22° proves the existence of amorphous carbon, which represents the abundant microporous structure distributed inside the sample after activation [42–44]. And with the further increase of the activation temperature, the intensity of the broad diffraction peak gradually

weakened and the peak width increased [45,46]. Corresponding to the previous SEM characterization results, it was found that a higher activation temperature would lead to the collapse of the carbon-based structure. The diffraction peak at 43° is closely related to the degree of graphitization of the carbon-based material, and the common diffraction peak of the three samples proves that the activated carbon materials after carbonization and activation have a certain intensity of graphitization characteristics [46]. In addition, there is no other obvious diffraction peak in the diffraction pattern, which proves the effective preparation of high-purity carbon-based materials.

Raman technology was further used to characterize the synthesized active carbon materials, and the results are shown in Fig. 3B. The spectral peaks located at 1341 cm^{-1} and 1574 cm^{-1} in the figure correspond to the D and G peaks of the carbon-based material, respectively. Where the D peak is related to the disorder and defects of the material, while the G peak is related to the order degree of the material [47–50]. The ratio of the two peaks can effectively reflect the order degree of the atomic arrangement of the material, and the larger the ratio is, the more defects in the material, which means the lower order degree [32,51]. The calculated I_D/I_G values of samples prepared at different activation temperatures are 1.01 (CF-800), 0.72 (CF-900) and 1.00 (CF-1000) respectively. The comparison results show that when the activation temperature is low, the carbon-based materials have more defects, and when the activation temperature increases from 800 °C to

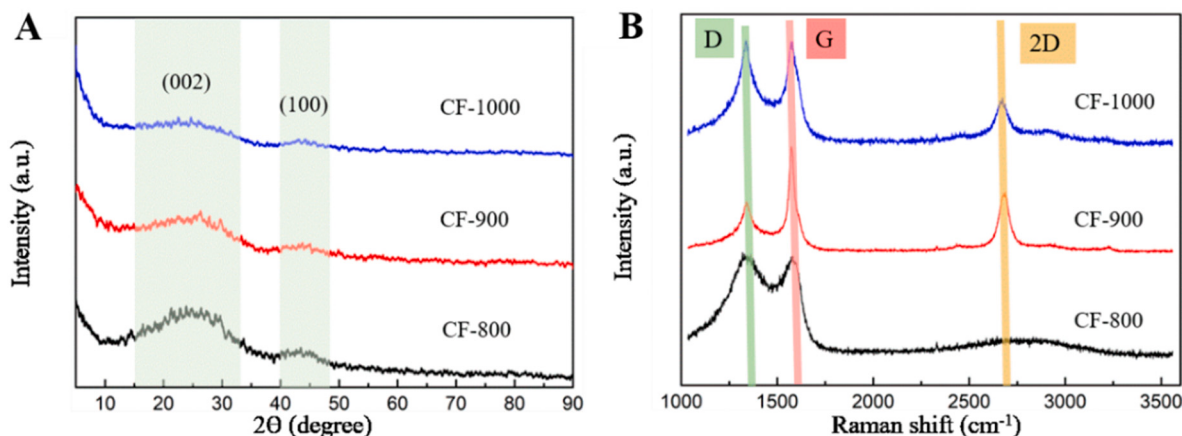


Fig. 3. (A) XRD patterns and (B) Raman spectrums of CF-800, CF-900 and CF-1000.

900 °C, the order degree of the prepared carbon materials is significantly improved, indicating that the graphitization degree is enhanced, which is beneficial to exhibit better electrical conductivity. However, when the activation temperature is further increased, the I_D/I_G ratio increases, which means that the excessive etching effect destroys the structure of the material, resulting in an increase of its defects. At the same time, the 2D peak at 2675 cm^{-1} is the characteristic peak of 3D few-layer graphene, the existence of this peak indicates that the activation process promotes the generation of 3D graphene structure, and the existence of the spatial structure of 3D graphene is beneficial to the improvement of the conductivity of the composite [52–54]. The conductivity test results showed in Fig. S3 can also prove that CF-900 has the highest conductivity, which the value can reach 71.73 S/m . From the above Raman test results, it can be seen that the three-dimensional hierarchical porous activated carbon material activated at 900 °C has the optimal graphitization degree, and the composite device prepared by this is expected to show better capacitance performance.

The activated carbon materials prepared at different activation temperatures were tested by N_2 adsorption and desorption to characterize the differences in specific surface area and pore size distribution of the respective materials, which results are shown in Fig. 4. First of all, the curves in Fig. A show that the samples prepared at the three activation temperatures show obvious adsorption characteristics below $P/P_0 = 0.99$ and all exhibit IV-type adsorption curves, and the curves appear slightly upturned when $P/P_0 > 0.9$, representing the presence of macropores in the material [55]. When the relative pressure is in the range of $P/P_0 = 0.45\text{--}0.99$, the adsorption-desorption curve shows a H4 hysteresis loop, indicating that there are a large number of mesopores and micropores in the sample, which also can be proved from the pore size distribution curve in Fig. 4B. In the lower relative pressure range, the curves are approximately linear, which is due to the existence of a large number of micropores in the material [56]. Comparing the three curves in Fig. 4A, the sample activated at 1000 °C has the most obvious hysteresis loop, which indicates that the sample prepared under higher temperature has abundant mesoporous structure [57]. According to the pore size distribution in Fig. 4B and the statistical results in Table S2, it can be known that the pore sizes of the samples activated at 900 and 1000 °C are mainly distributed in the range of 0.5–2.0 nm and 2.0–5.0 nm, which correspond to the microporous and mesoporous structures in carbon materials, respectively [55]. However, the samples activated at 800 °C are dominated by micropores $<1\text{ nm}$ and lack the pore structure of mesopore size. This is because at a higher activation temperature, more active ions in the activator are embedded into the carbon matrix, which enhances the etching effect. It will lead to the destruction of part of the microporous structure, and then interconnected to form mesopores and macropores [58]. At the same time, the space between the

carbon layers becomes larger, which increases the total pore volume of the material. The above results can show that the mesoporous structure introduced through the carbonization and activation process has obvious adsorption characteristics, and it can also be seen that the porosity of the carbon material is affected by the activation temperature, that is, with the increase of the activation temperature, the micropores in the carbon skeleton are gradually destroyed, and the mesopores and macropores are formed after being interconnected. However, according to literature reports, the mesoporous structure with a size between 2 and 5 nm is more conducive to the rapid transport of electrolytes. Therefore, based on the above test results, electrode materials with more mesoporous proportions prepared at high temperature are more suitable for the preparation of supercapacitor electrodes.

The etched porous carbon material after activation was assembled into a traditional button-type supercapacitor, and its electrochemical performance was tested by an electrochemical workstation under a two-electrode system. The electrolyte was selected as a 1 M H_2SO_4 solution. Fig. 5A–C show the CV curves of samples prepared under different temperatures. The voltage window of the test is 0–0.8 V, and the scan rate is 2, 5, 10, 20, 50 and $100\text{ mV}\cdot\text{s}^{-1}$, respectively. Each curve shows a good quasi-rectangular shape, indicating that the material has typical electric double-layer capacitance characteristics, and after gradually increasing the scan speed, the CV curve has no obvious deformation, indicating that the material has a good rate capability. The specific capacitances of the three samples were calculated to be 234, 229 and $215\text{ F}\cdot\text{g}^{-1}$ at a scan speed of $2\text{ mV}\cdot\text{s}^{-1}$, respectively. It can be seen that the specific capacitance of the CF-800 is the largest. This is because the sample activated at low temperature has a large proportion of micropores. The electrolyte ions can be effectively embedded into the activated carbon at a lower scan rate to achieve ion adsorption, resulting in a larger specific capacitance. However, as shown in Fig. 5A, with the increase of the scan speed, the specific capacitance decreases more obviously, while the test curves of CF-900 and CF-1000 still maintain a good rectangular shape, which proves that the samples after high temperature activation have excellent rate performance and specific capacitance retention. The maintenance of performance comes from the excellent hierarchical porous structure. Under the scanning rate of $100\text{ mV}\cdot\text{s}^{-1}$, he calculated specific capacitance of the three samples 134, 146 and $159\text{ F}\cdot\text{g}^{-1}$, and the capacitance retention rates are 57 %, 64 % and 74 %, respectively. By comparison the above data, it is found that the electrolyte ions cannot rapidly diffuse to the microporous surface of the carbon materials at high scan rate, which degrades the rate capability of the sample activated at low temperature.

The charge-discharge performance of the prepared materials was characterized by electrochemical GCD curves, and the results are shown in Fig. 6. It can be seen that the test curves of different materials are in

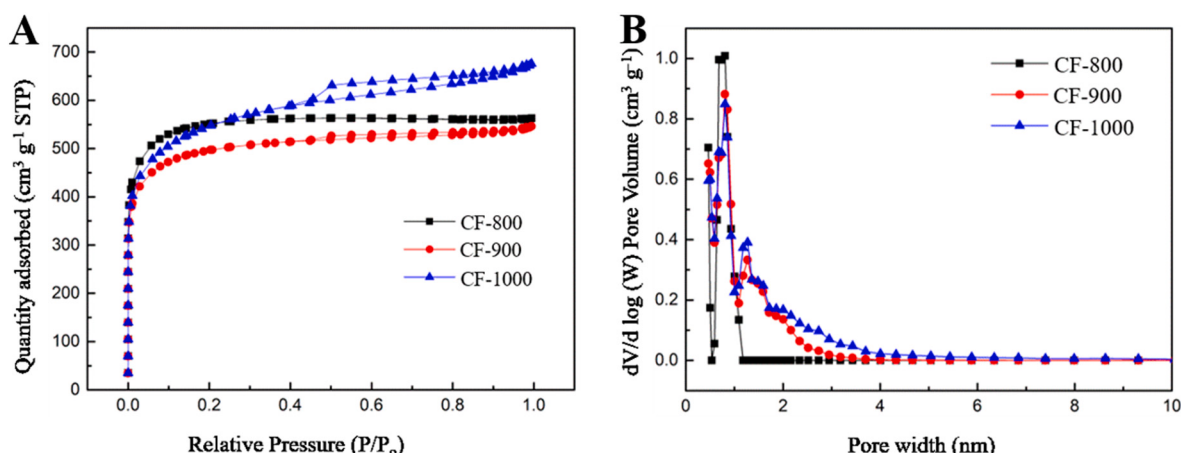


Fig. 4. (A) N_2 adsorption-desorption isotherms and (B) Pore size distributions of CF-800, CF-900 and CF-1000.

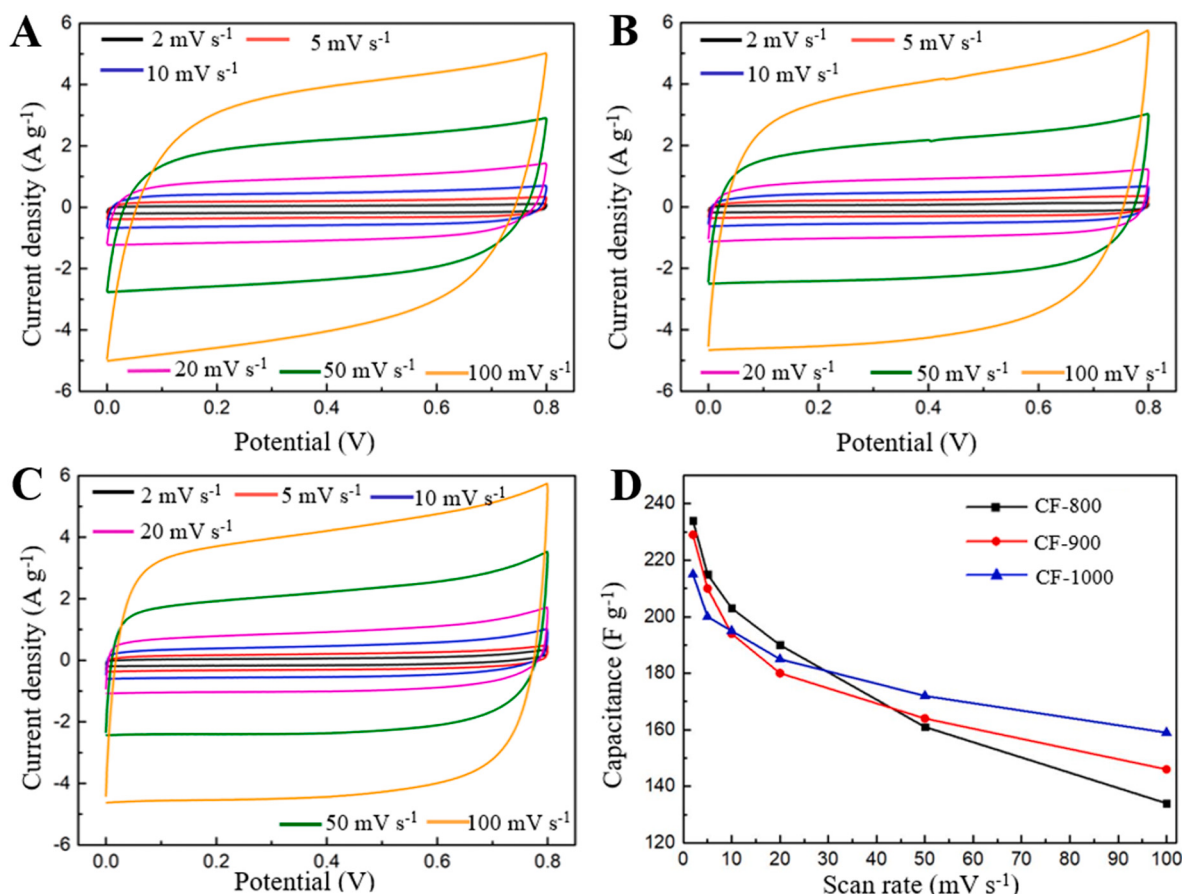


Fig. 5. CV curves of (A) CF-800, (B) CF-900, (C) CF-1000 electrodes under different scan rates from 2 to 100 mV·s⁻¹, (D) Specific capacitance at varied scan rates.

the shape of a symmetrical isosceles triangle, which proves that the activated carbon has good capacitance and charge-discharge reversibility, and there is no obvious voltage drop during discharge, indicating that the material has excellent conductivity and there is no partial voltage loss caused by additional contact resistance [59,60]. The calculated specific capacitances of CF-800, CF-900 and CF-1000 are 215 F·g⁻¹, 200 F·g⁻¹ and 202 F·g⁻¹ respectively with the current density is 0.2 A·g⁻¹. Consistent with the previous CV test results, the samples activated at lower temperature showed the highest capacitive performance, and the higher proportion of micropores allowed the electrolyte ions to be fully diffused at small current densities. The slow diffusion rate within the porous structure makes the charge-discharge time of this sample longer compared to others. When the current density is further increased to 10 A·g⁻¹, the specific capacitance of CF-800 can hardly be measured. This is because the sample activated at lower temperature lacks a mesoporous structure which is conducive to electrolyte diffusion. At high current density, the contact area between electrolyte ions and functional carbon materials is reduced, which decreases the adsorbed charge on the surface of carbon-based materials, resulting in low specific capacitance output. CF-900 showed a good linear relationship of voltage with time, and there was no obvious voltage drop at high current density. According to the pore distribution curves, CF-900 and CF-1000 have high proportion of mesopore and macropore due to the enhancement of etching intensity during the activation process, and CF-1000 is the highest one. The larger pore size facilitates the rapid transfer of electrolyte in the electrode material. With high current density, the specific capacitance of the capacitor is improved with the increase of activation temperature. On the contrary, with low activation temperature (800 °C), the electrode material has relative high micropore percentage so that electrolyte ions have to take longer time to diffuse into pores to realize charge adsorption. Therefore, compare to CF-900 and

CF-1000, CF-800 exhibits higher specific capacitance at low current density, whereas the other two demonstrate higher specific capacitance at high current density.

The dynamic information of the charge transfer between the electrode material and the electrolyte is characterized by EIS, the test frequency range is from 0.01 Hz to 100 kHz, and the open circuit potential is 5 mV. The test results are shown in Fig. 7A, in which the inset is the equivalent circuit diagram of the circuit, where R_s is the series resistance of the electrode, including the electrode material resistance, the electrolyte resistance and the contact resistance between the electrode and the current collector. Which size is reflected by the intercept of the semicircle in the high frequency region of the EIS curve on the real axis [61]. It can be seen from the test results that the higher activation temperature can lead to lower electrode resistance. The curve in the low frequency region is nearly linear, and the slope of the curve is closely related to the diffusion performance of electrolyte ions [62]. It can be seen from the result that compared with CF-800, the sample prepared at a higher activation temperature shows a higher straight line slope, among which the slope of CF-900 curve was the largest, indicating that the material has better electrolyte ion diffusion efficiency, which is benefited from the existence of hierarchical porous structures in the samples activated at high temperatures, thus in turn resulted in better capacitive performance [63]. The slight increase in R_s of CF-1000 is probably due to the structural collapse at high temperature.

From the results of the previous electrochemical characterization test, it can be concluded that the carbon electrode activated at 900 °C has the best electrical conductivity and relatively good capacitance performance. Furthermore, the electrochemical stability of the all-solid-state flexible supercapacitor composed of this electrode and PVA/H₂SO₄ gel electrolyte was characterized. Fig. 7B shows the cyclic charge-discharge test results of the device at a current density of 10 A·g⁻¹. It

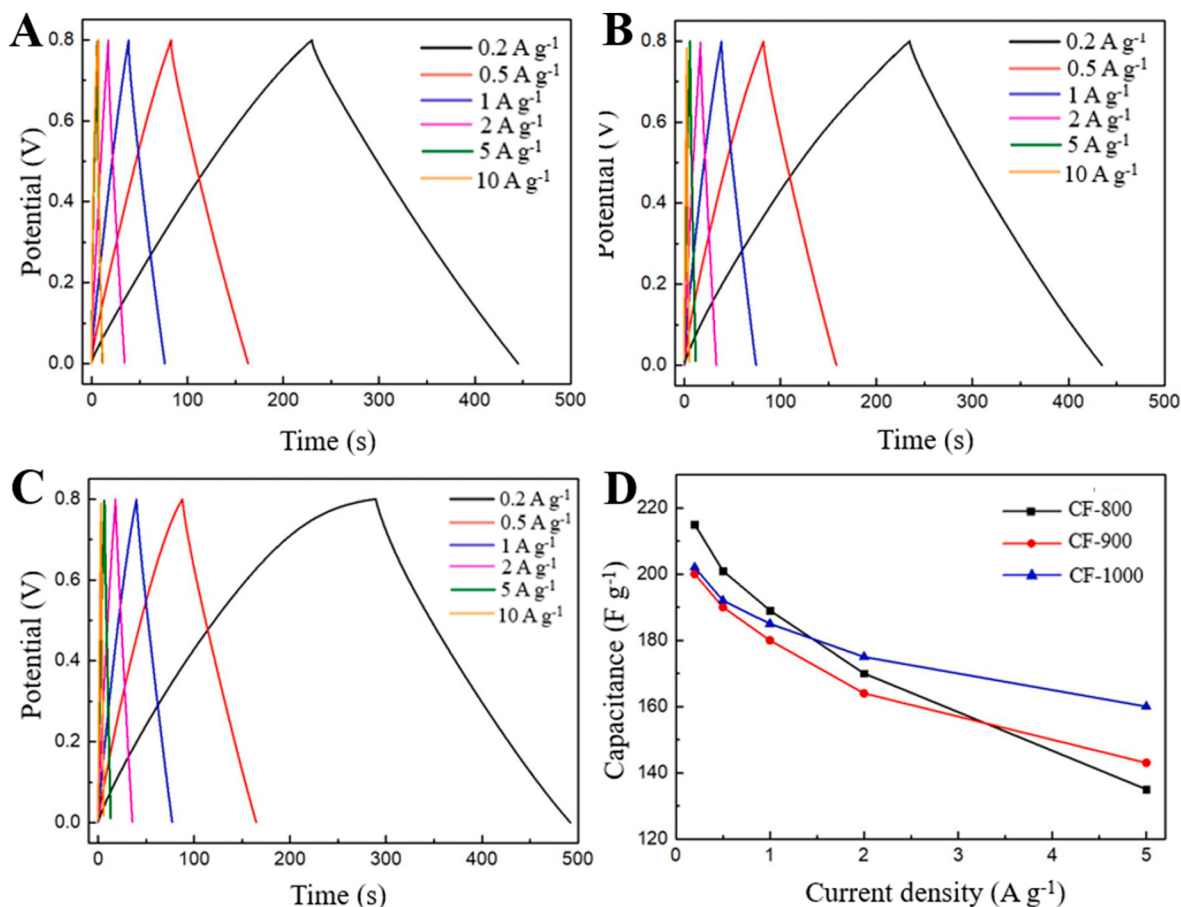


Fig. 6. (A-C) GCD curves of the CF-800, CF-900 and CF-1000 electrodes under different current densities from 0.2 to 10 A g⁻¹, (D) Specific capacitance at varied current densities.

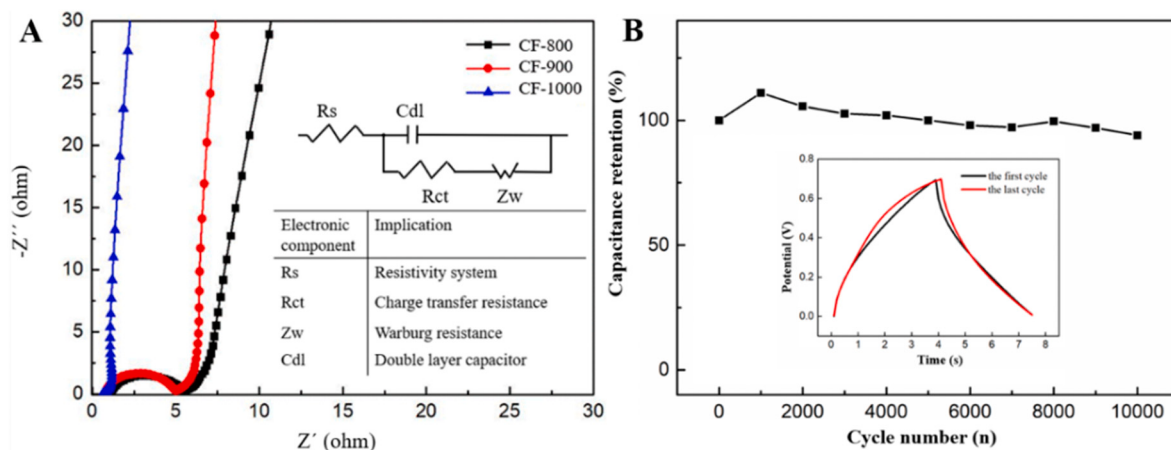


Fig. 7. (A) Nyquist plots of the CF-800, CF-900 and CF-1000 electrodes, (B) Cycling stability of CF-900 electrode at a current density of 10 A g⁻¹, the inset shows GCD curves for initial and final cycle.

can be seen that the specific capacitance of the device shows a trend of first increasing and then decreasing with the cycle period. The increase in the specific capacitance in the front section is due to the repeated intercalation and deintercalation of the PVA/H₂SO₄ electrolyte in the cycle test, which can fully activate the electrode material and alleviates the poor conductive characteristics of the electrolyte in the initial test [64,65]. After 10,000 cycle tests, the specific capacitance retention rate is 94 % of the initial value. Combined with the comparison of the charge-discharge curves before and after 10,000 cycles in the inset, it can be

seen that the device can still maintain stable charge-discharge characteristics in the long-cycle test. Which indicating that the flexible all-solid-state supercapacitor has good electrochemical stability.

In order to further explore the application potential of coconut silk-based activated carbon materials in the field of flexible supercapacitors. The electrochemical and mechanical properties of the flexible supercapacitor were investigated by electrochemical workstation and extensometer. Fig. 8 shows the measured CV curves of the assembled flexible supercapacitors at different scan speeds, and their specific capacitances

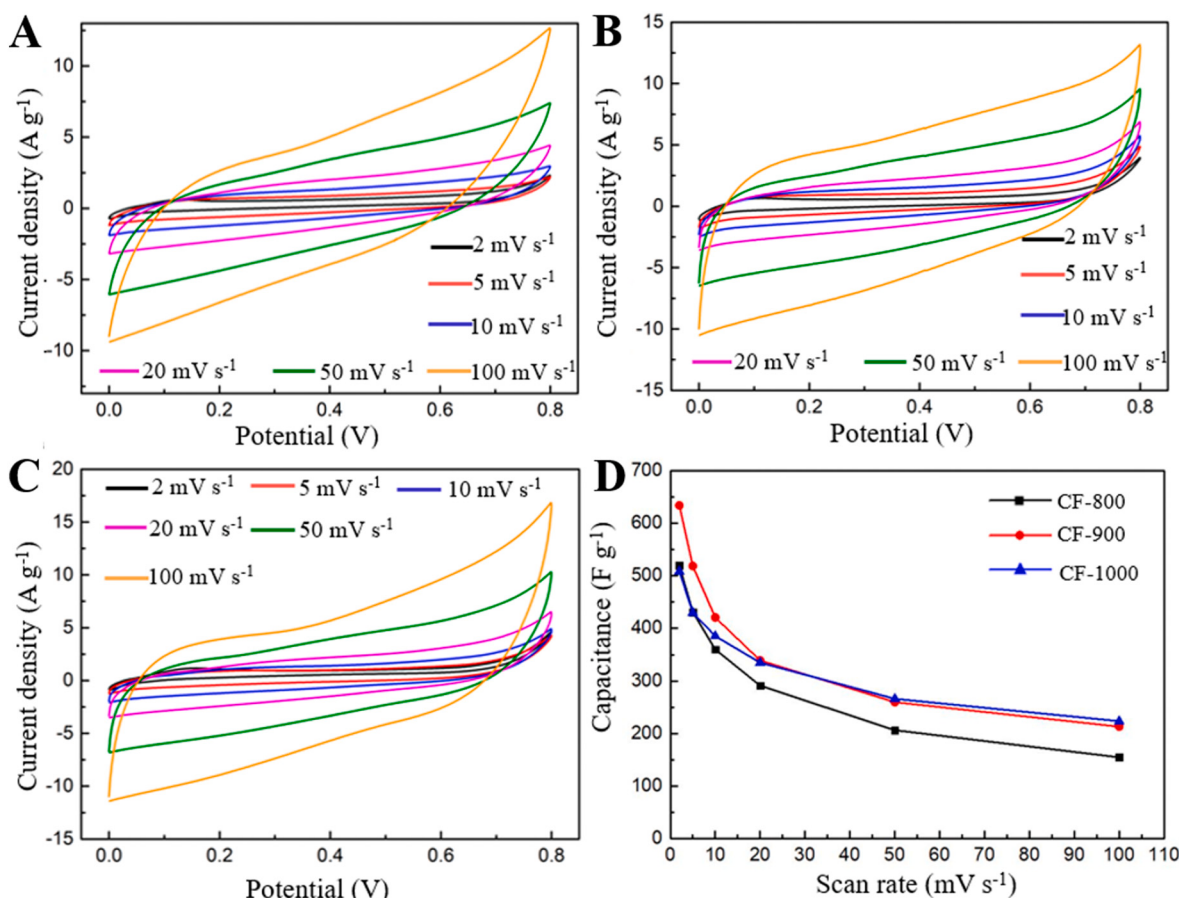


Fig. 8. CV curves of all-solid-state flexible supercapacitors based on (A) CF-800, (B) CF-900, (C) CF-1000 electrode under different scan rates from 2 to 100 mV s⁻¹, (D) Specific capacitance at varied scan rates.

are calculated to be 519.5 F g⁻¹ (CF-800), 634.2 F g⁻¹ (CF-900), and 508.5 F g⁻¹ (CF-1000), respectively. All-solid-state flexible supercapacitors in this work exhibit higher capacitive performance than that in CF-900, SVS-900 and SIS-800 in traditional supercapacitors (229 F g⁻¹, 248 F g⁻¹, 223 F g⁻¹). It is largely due to the fact that PVA gel electrolyte is a polymer rich in hydroxyl groups, which can promote much more effective ion exchange between the electrolyte and the electrode material [66,67]. It can be seen that CF-900 exhibits the most excellent capacitance performance. Although the sample has a relatively low specific surface area in the previous BET test, its reasonable hierarchical porous structure provides the impetus for the diffusion of solid electrolyte ions, which increases the adsorption sites of the carbon electrode. At the same time, it can be seen from the data that the CV curve of CF-900 presents a more standard rectangle shape, which means that the composite device has good electric double layer capacitance characteristics and excellent rate capability.

When carbon materials are activated with KOH, oxygen-containing functional groups are generated on the surface of the electrode, resulting in enhanced surface reactions between the interfaces [68]. The presence of oxygen greatly improves the wettability and electrochemically active sites of the electrode surface, thus contributing to part of the pseudocapacitive capacitance. Therefore, from the GCD curves shown in Fig. 9, the charge-discharge curves of the three devices all show weak curvature bending at the scan rate of 1 A g⁻¹. Consistent with the CV test results, the CF-900 activated carbon electrode exhibited better capacitance performance, with a specific capacitance of 631 and 326 F g⁻¹ at current densities of 1 A g⁻¹ and 10 A g⁻¹, respectively. It can be seen that compared with micropores, which limit the diffusion of electrolyte ions, macropores reduce the adsorption sites of electrolyte ions, the

hierarchically porous structure is more beneficial to achieve higher capacitive performance [69]. At the same time, as shown in Fig. 10A, the CF-900-based all-solid-state flexible supercapacitor can exhibit higher energy density and power density than traditional button supercapacitors, and the maximum values can respectively reach 10.73 Wh kg⁻¹ and 3500.14 W kg⁻¹. The specific comparison data are shown in Table S3.

In order to further evaluate the charge transport performance of coconut silk-based carbon materials in the all-solid-state supercapacitor system, three groups of materials were tested by EIS, and the test parameters were kept the same as those of the previous button supercapacitor test, the results are shown in Fig. 10B. The enlarged view of the high-frequency region curve is shown in the inset Fig. 10. It can be seen that the CF-900 curve has the smallest intercept with the real part of the Z-axis, indicating that the device has lower electrode resistance and higher charge transfer capability. Also, the higher slope of the test curve in the low-frequency region indicates that the device has a higher ion diffusion ability, which is conducive to the adsorption of charge on the electrode surface. These excellent performances are derived from the regular hierarchical porous structure and higher degree of graphitization of CF-900.

Besides excellent energy storage performance, good mechanical stability is also a necessary condition for the development of flexible energy storage devices. Therefore, in order to effectively evaluate the application potential in wearable electronic devices of the all-solid-state flexible supercapacitors prepared in this work, different bending angles (0°, 45°, 90°, 135° and 180°) were performed on the CF-900 assembled devices under the electrochemical CV test. The results are shown in Fig. 11A. Except for the slight deformation of the CV curve after the fully

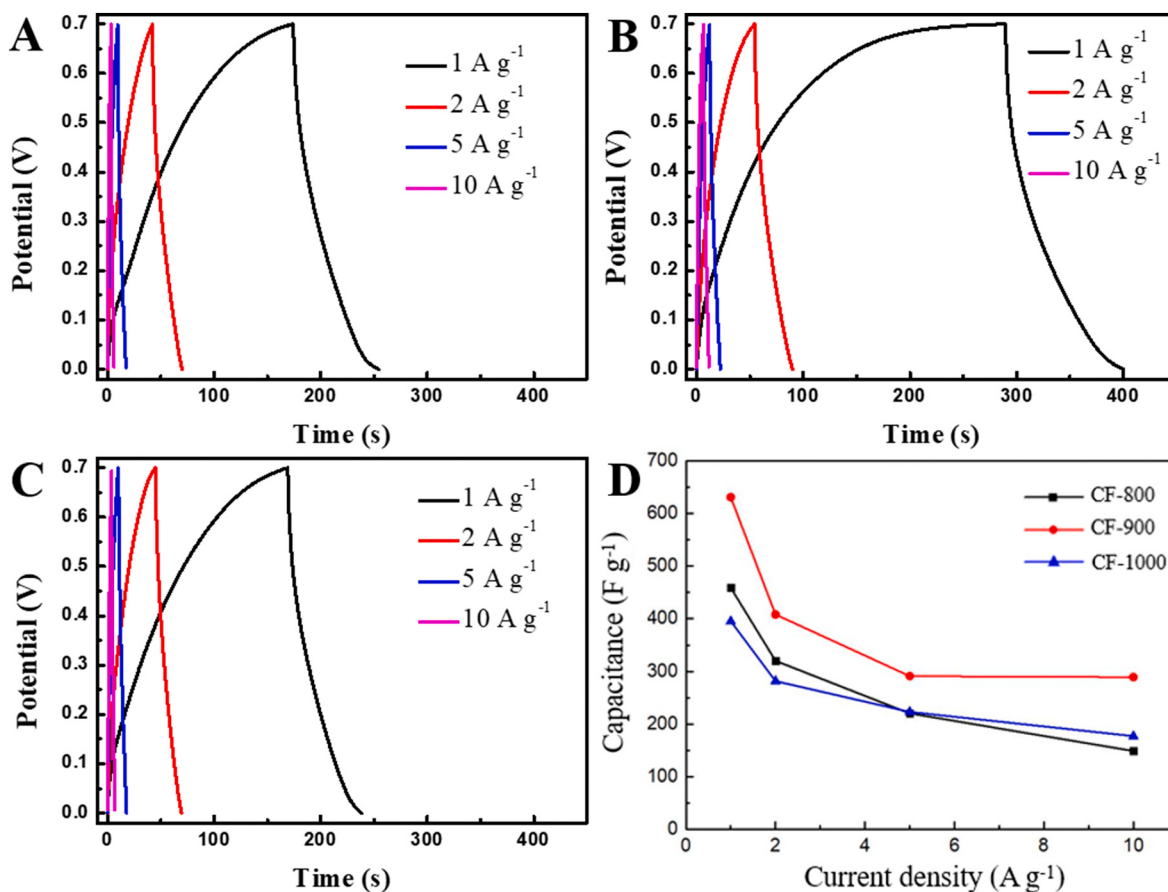


Fig. 9. GCD curves of all-solid-state flexible supercapacitors based on (A) CF-800, (B) CF-900, (C) CF-1000 electrode under different current densities from 1 to 10 A g⁻¹, (D) Specific capacitance at varied current densities.

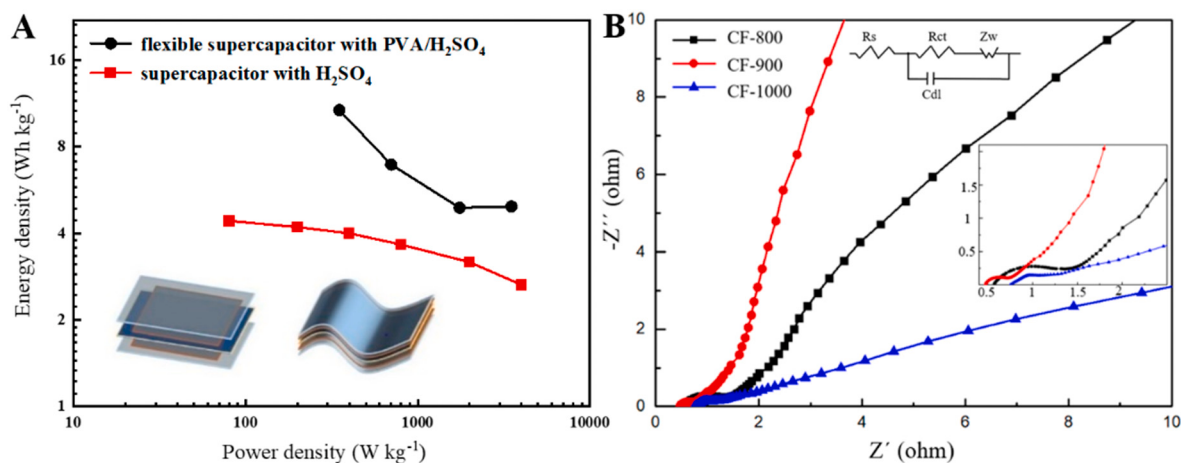


Fig. 10. (A) Comparison of Ragone plot between button supercapacitor and all-solid-state flexible supercapacitor based on CF-900 electrode. (B) Nyquist plots of the all-solid-state flexible supercapacitors based on CF-800, CF-900 and CF-1000 electrode, the inner pictures are equivalent circuit diagrams and enlarged view of high frequency curves.

folded condition, the other curves almost coincide with the initial state. The capacitance of the device after different bending angles are 113.8 %, 111.1 %, 102.3 % and 99.5 % of the initial value, respectively. At the small bending angle, the increase of the device capacitance may come from the fact that the spatial structure of the carbon material is squeezed during bending, and the gel electrolyte fully penetrates into the micropores of the electrode material under the action of pressure, which increases the adsorption of the electrode material and the electrolyte ions.

In addition, the bending action leads to the generation of new cracks or sections in the activated carbon framework, which increases the adsorption sites between the electrolyte and the activated carbon material, which in turn leads to an increase in the capacitance of the flexible device [70,71]. Then, the device was subjected to a bending cycle test to characterize the mechanical durability of the device. In the experiment, 140° was selected as the bending angle, 10,000 times as the bending cycle, and sampling records were performed every 1000 times of

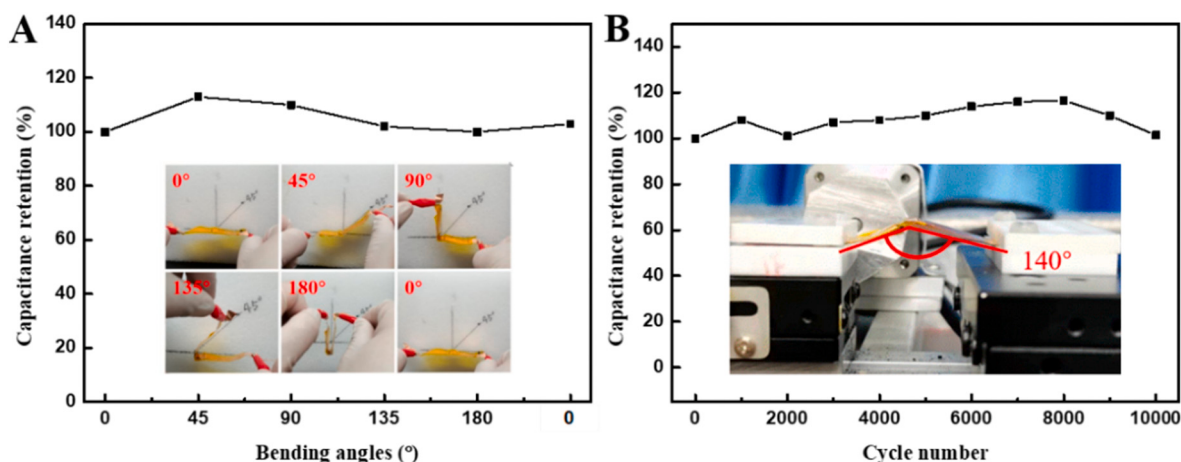


Fig. 11. Mechanical stability test of all-solid-state flexible supercapacitor based on CF-900 electrode. (A) Specific capacitance retention curves under different bending angles, (B) Specific capacitance retention curves under different bending cycles (140° was selected as the bending angle).

bending. The statistical results are shown in Fig. 11B. During the bending process, the specific capacitance of the device increased first and then decreased. After 10,000 bending tests, the specific capacitance was 101.5 % of the initial value. The reason for this phenomenon is consistent with the effect of different bending angles on the capacitance performance in the previous experiments, that is, the bending operation enhances the contact ability between the electrolyte and the activated carbon material, and is accompanied by the generation of a new adsorption interface [72]. With the increase of the bending cycle in the latter process, the structure of the carbon skeleton is gradually destroyed, resulting in a weak attenuation of the capacitance, but even so, the CF-900-based all-solid-state supercapacitor can still maintain better capacitance and stable mechanical properties among similar energy storage devices, which showing the broad application prospects of coconut silk long fiber biomass materials in the field of flexible energy storage [70,73].

4. Conclusion

In conclusion, an activated carbon electrode with a hierarchical porous structure was prepared in this work by simple carbonization and KOH activation using long-fiber coconut silk with vascular bundle structure as the source material. In the experiment, the pore structure and conductive properties of the electrode material were effectively regulated by adjusting the activation temperature of KOH. The results showed that the symmetric all-solid-state flexible supercapacitor with activated carbon material prepared by activation at 900 °C as electrode and PVA/H₂SO₄ as gel electrolyte showed an electrode specific capacitance of 634 F·g⁻¹ at 2 mV·s⁻¹, along with an energy density of 10.73 Wh·kg⁻¹ and a power density of 3500.14 W·kg⁻¹, which is the highest capacitance performance among similar biomass-derived carbon flexible supercapacitors. At the same time, the flexible all-solid-state supercapacitor also has excellent mechanical stability, and its capacitance retention rate can reach 101.5 % after 10,000 bending experiments at an inner angle of 140°. The excellent performance mainly comes from the following three aspects: 1. The samples prepared under this condition have high specific surface area and rich hierarchical porous structure, which is beneficial to improve the contact between the electrode material and the electrolyte, and improve the adsorption capacity of ions, thereby increasing the charge storage density. 2. The three-dimensional carbon skeleton has a reasonable distribution ratio of micropores, mesopores and macropores, and the pores are interconnected. This structure provides an effective path and power for the penetration of electrolytes and the diffusion of ions. 3. The combination of porous carbon framework and gel-like electrolyte enables it to

withstand greater stress under mechanical deformation to ensure the mechanical stability and durability of the device. This experimental work demonstrates the advantages and potential of long-fiber biomass carbon materials with vascular bundle structure in the field of preparing flexible supercapacitors, which provides an effective guidance for the energy storage design of wearable electronic devices in the future.

CRediT authorship contribution statement

Rongke Sun: Methodology, Investigation, Data curation, Writing—original draft preparation.

Xiao Zhang: Investigation, Data curation, Writing preparation.

Zejian Chen: Investigation, Data curation.

Yanqing Ma: Validation, Writing-review & editing, Supervision.

Lei Ma: Conceptualization, Supervision, Methodology, Validation, Writing- review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.est.2023.107410>.

References

- [1] Q. Zhang, C. Xin, F. Shen, Y. Gong, Y. Zi, H. Guo, Z. Li, Y. Peng, Q. Zhang, Z. L. Wang, Human body IoT systems based on the triboelectricity effect: energy harvesting, sensing, interfacing and communication, *Energy Environ. Sci.* 15 (9) (2022) 3688–3721.
- [2] F. Qiu, Y. Huang, G. He, C. Luo, X. Li, M. Wang, Y. Wu, in: *A Lignocellulose-based Neutral Hydrogel Electrolyte for High-voltage Supercapacitors With Overlong Cyclic Stability* 363, 2020, p. 137241.

- [3] X. Li, Y. Tang, J. Song, W. Yang, M. Wang, C. Zhu, W. Zhao, J. Zheng, Y. Lin, in: Self-supporting activated carbon/carbon nanotube/reduced graphene oxide flexible electrode for high performance supercapacitor 129, 2018, pp. 236–244.
- [4] Z. Li, D. Guo, Y. Liu, H. Wang, L. Wang, in: Recent advances and challenges in biomass-derived porous carbon nanomaterials for supercapacitors 397, 2020, p. 125418.
- [5] S. Hui, Z. Ying, X. Lin, J. Sun, Y. Wang, Q. Fu, J. Li, in: Novel scalable freeze-pore-forming strategy for constructing hierarchically porous carbon materials for supercapacitors 846, 2020, p. 156235.
- [6] Z. Yu, L. Tetard, L. Zhai, J. Thomas, in: Supercapacitor Electrode Materials: Nanostructures From 0 to 3 Dimensions 8 (3), 2015, pp. 702–730.
- [7] X. Jiang, T. Chen, B. Liu, R. Sun, J. Fu, X. Jiang, P. Cui, Z. Liu, W. Han, in: Enhancing Energy Storage Capacity of Iron Oxide-based Anodes by Adjusting Fe (II/III) Ratio in Spinel Crystalline 32 (39), 2021, p. 395705.
- [8] J. Sun, C. Wu, X. Sun, H. Hu, C. Zhi, L. Hou, C. Yuan, in: Recent progresses in high-energy-density all pseudocapacitive-electrode-materials-based asymmetric supercapacitors 5 (20), 2017, pp. 9443–9464.
- [9] J. Wang, X. Zhang, Z. Li, Y. Ma, L. Ma, in: Recent progress of biomass-derived carbon materials for supercapacitors 451, 2020, p. 227794.
- [10] Z. Wang, D. Shen, C. Wu, S. Gu, in: State-of-the-art on the Production and Application of Carbon Nanomaterials From Biomass 20 (22), 2018, pp. 5031–5057.
- [11] Y. Bai, B. Shen, S. Zhang, Z. Zhu, S. Sun, J. Gao, B. Li, Y. Wang, R. Zhang, F. Wei, in: Storage of Mechanical Energy Based on Carbon Nanotubes With High Energy Density and Power Density 31 (9), 2019, p. 1800680.
- [12] V. Strauss, K. Marsh, M.D. Kowal, M. El-Kady, R.B. Kaner, in: A simple route to porous graphene from carbon nanodots for supercapacitor applications 30 (8), 2018, p. 1704449.
- [13] L. Zhang, X.S. Zhao, in: Carbon-based Materials as Supercapacitor Electrodes 38 (9), 2009, pp. 2520–2531.
- [14] Y. Yang, in: A Mini-review: Emerging All-solid-state Energy Storage Electrode Materials for Flexible Devices 12 (6), 2020, pp. 3560–3573.
- [15] N. Guo, S. Zhang, L. Wang, D. Jia, Application of Plant-based Porous Carbon for Supercapacitors 36 (2), 2020.
- [16] Y. Zhang, S. Yu, G. Lou, Y. Shen, H. Chen, Z. Shen, S. Zhao, J. Zhang, S. Chai, Q. Zou, in: Review of macroporous materials as electrochemical supercapacitor electrodes 52 (19), 2017, pp. 11201–11228.
- [17] L. Dong, G. Liang, C. Xu, W. Liu, Z.-Z. Pan, E. Zhou, F. Kang, Q.-H. Yang, in: Multi hierarchical construction-induced superior capacitive performances of flexible electrodes for wearable energy storage 34, 2017, pp. 242–248.
- [18] R. Saidur, E. Abdelaziz, A. Demiras, M. Hossain, S. Mekhilef, in: A review on biomass as a fuel for boilers 15 (5), 2011, pp. 2262–2289.
- [19] L. Jiang, L. Sheng, Z. Fan, in: Biomass-derived Carbon Materials With Structural Diversities and Their Applications in Energy Storage 61 (2), 2018, pp. 133–158.
- [20] Y. Zhang, S. Liu, X. Zheng, X. Wang, Y. Xu, H. Tang, F. Kang, Q.H. Yang, J. Luo, in: Biomass organs control the porosity of their pyrolyzed carbon 27 (3), 2017, p. 1604687.
- [21] C. Qin, H. Wang, X. Yuan, T. Xiong, J. Zhang, J. Zhang, in: Understanding structure-performance correlation of biochar materials in environmental remediation and electrochemical devices 382, 2020, p. 122977.
- [22] M.S. Priya, P. Divya, R. Rajalakshmi, in: A review status on characterization and electrochemical behaviour of biomass derived carbon materials for energy storage supercapacitors 16, 2020, p. 100243.
- [23] Y. Zhang, J. He, Z. Gao, X. Li, in: Converting Eggs to Flexible, All-solid Supercapacitors 65, 2019, p. 104045.
- [24] Q. Sun, D. Yu, F. Mo, M. Wu, Y. Liu, X. Dong, in: Wool textile-derived nitrogen-doped porous carbon cloth for a binder-free electrode material for high-performance flexible solid-state supercapacitors 56 (3), 2021, pp. 2412–2424.
- [25] P.-A. Le, V.-T. Nguyen, S.K. Sahoo, T.Y. Tseng, K.-H. Wei, in: Porous carbon materials derived from areca palm leaves for high performance symmetrical solid-state supercapacitors 55 (24), 2020, pp. 10751–10764.
- [26] Z. Yang, M. Xiang, W. Zhu, J. Hui, H. Qin, in: Biomass heteroatom carbon/cerium dioxide composite nanomaterials electrode for high-performance supercapacitors 8 (17), 2020, pp. 6675–6681.
- [27] H. Bi, X. He, H. Zhang, H. Li, N. Xiao, J. Qiu, in: N, P co-doped hierarchical porous carbon from rapeseed cake with enhanced supercapacitance 170, 2021, pp. 188–196.
- [28] Y. Wang, R. Liu, Y. Tian, Z. Sun, Z. Huang, X. Wu, B. Li, in: Heteroatoms-doped hierarchical porous carbon derived from chitin for flexible all-solid-state symmetric supercapacitors 384, 2020, p. 123263.
- [29] D. Khalafallah, X. Quan, C. Ouyang, M. Zhi, Z. Hong, in: Heteroatoms doped porous carbon derived from waste potato peel for supercapacitors 170, 2021, pp. 60–71.
- [30] A. Khan, R.A. Senthil, J. Pan, S. Osman, Y. Sun, X. Shu, in: A new biomass derived rod-like porous carbon from tea-waste as inexpensive and sustainable energy material for advanced supercapacitor application 335, 2020, p. 135588.
- [31] W. Li, Z. Chen, H. Yu, J. Li, S. Liu, in: Wood-Derived Carbon Materials and Light-Emitting Materials 33 (28), 2021, p. 2000596.
- [32] J. Wang, Z. Li, S. Yan, X. Yu, Y. Ma, L. Ma, in: Modifying the microstructure of algae-based active carbon and modelling supercapacitors using artificial neural networks 9 (26), 2019, pp. 14797–14808.
- [33] D. He, W. Zhao, P. Li, Z. Liu, H. Wu, L. Liu, K. Han, L. Liu, Q. Wan, F.K. Butt, X. Qu, in: Bifunctional biomass-derived 3D nitrogen-doped porous carbon for oxygen reduction reaction and solid-state supercapacitor 465, 2019, pp. 303–312.
- [34] F. Liu, Y. Gao, C. Zhang, H. Huang, C. Yan, X. Chu, Z. Xu, Z. Wang, H. Zhang, X. Xiao, in: Highly microporous carbon with nitrogen-doping derived from natural biowaste for high-performance flexible solid-state supercapacitor 548, 2019, pp. 322–332.
- [35] W. Du, Z. Zhang, L. Du, X. Fan, Z. Shen, X. Ren, Y. Zhao, C. Wei, S. Wei, in: Designing synthesis of porous biomass carbon from wheat straw and the functionalizing application in flexible, all-solid-state supercapacitors 797, 2019, pp. 1031–1040.
- [36] Z. Li, S. Gao, H. Mi, C. Lei, C. Ji, Z. Xie, C. Yu, J. Qiu, in: High-energy Quasi-solid-state Supercapacitors Enabled by Carbon Nanofoam From Biowaste and High-voltage Inorganic Gel Electrolyte 149, 2019, pp. 273–280.
- [37] L. Sun, G. Song, Y. Sun, Q. Fu, C. Pan, in: One-step Construction of 3D N/P-codoped Hierarchically Porous Carbon Framework In-situ Armored Mn₃O₄ Nanoparticles for High-performance Flexible Supercapacitors 333, 2020, p. 135496.
- [38] Z. Shang, X. An, H. Zhang, M. Shen, F. Baker, Y. Liu, L. Liu, J. Yang, H. Cao, Q. Xu, H. Liu, Y. Ni, in: Houttuynia-derived nitrogen-doped hierarchically porous carbon for high-performance supercapacitor 161, 2020, pp. 62–70.
- [39] Y. Liu, Z. Xiao, Y. Liu, L.-Z. Fan, in: Biowaste-derived 3D honeycomb-like porous carbon with binary-heteroatom doping for high-performance flexible solid-state supercapacitors 6 (1), 2018, pp. 160–166.
- [40] Y. Ding, T. Wang, D. Dong, Y. Zhang, in: Using biochar and coal as the electrode material for supercapacitor applications 7, 2020, p. 159.
- [41] Y. Wang, Z. Zhao, W. Song, Z. Wang, X. Wu, in: From biological waste to honeycomb-like porous carbon for high energy density supercapacitor 54 (6), 2019, pp. 4917–4927.
- [42] S. Liu, Y. Xu, J. Wu, J. Huang, in: Celery-derived porous carbon materials for superior performance supercapacitors 3 (18), 2021, pp. 5363–5372.
- [43] G. Zhu, L. Ma, H. Lv, Y. Hu, T. Chen, R. Chen, J. Liang, X. Wang, Y. Wang, C. Yan, Z. Tie, Z. Jin, J. Liu, Pine needle-derived microporous nitrogen-doped carbon frameworks exhibit high performances in electrocatalytic hydrogen evolution reaction, in: 9 (3), 2017, pp. 1237–1243.
- [44] Y.S. Yun, S.Y. Cho, J. Shim, B.H. Kim, S.J. Chang, S.J. Baek, Y.S. Huh, Y. Tak, Y. W. Park, S. Park, H.J. Jin, in: Microporous carbon nanoplates from regenerated silk proteins for supercapacitors 25 (14), 2013, pp. 1993–1998.
- [45] N. Zhao, P. Zhang, D. Luo, W. Xiao, L. Deng, F. Qiao, in: Direct production of porous carbon nanosheets/particle composites from wasted litchi shell for supercapacitors 788, 2019, pp. 677–684.
- [46] G. Lin, Q. Wang, X. Yang, Z. Cai, Y. Xiong, B. Huang, in: Preparation of phosphorus-doped porous carbon for high performance supercapacitors by one-step carbonization 10 (30), 2020, pp. 17768–17776.
- [47] G. Gou, F. Huang, M. Jiang, J. Li, Z. Zhou, in: Hierarchical porous carbon electrode materials for supercapacitor developed from wheat straw cellulosic foam 149, 2020, pp. 208–216.
- [48] J. Zhu, D. Xu, C. Wang, W. Qian, J. Guo, F. Yan, in: Ferric citrate-derived N-doped hierarchical porous carbons for oxygen reduction reaction and electrochemical supercapacitors 115, 2017, pp. 1–10.
- [49] W. Lu, X. Cao, L. Hao, Y. Zhou, Y. Wang, in: Activated carbon derived from pitaya peel for supercapacitor applications with high capacitance performance 264, 2020, p. 127339.
- [50] F.R.M.S. Raj, N.V. Jaya, G. Boopathi, D. Kalpana, A. Pandurangan, in: S-doped activated mesoporous carbon derived from the Borassus flabellifer flower as active electrodes for supercapacitors 240, 2020, p. 122151.
- [51] X. Tian, S. Zhu, J. Peng, Y. Zuo, G. Wang, X. Guo, N. Zhao, Y. Ma, L. Ma, in: Synthesis of micro-and meso-porous carbon derived from cellulose as an electrode material for supercapacitors 241, 2017, pp. 170–178.
- [52] J. Li, K. Han, D. Wang, Z. Teng, Y. Cao, J. Qi, M. Li, M. Wang, in: Fabrication of high performance structural N-doped hierarchical porous carbon for supercapacitors 164, 2020, pp. 42–50.
- [53] S. Dong, X. He, H. Zhang, X. Xie, M. Yu, C. Yu, N. Xiao, J. Qiu, in: Surface modification of biomass-derived hard carbon by grafting porous carbon nanosheets for high-performance supercapacitors 6 (33), 2018, pp. 15954–15960.
- [54] D. Mohapatra, G. Dhakal, M.S. Sayed, B. Subramanya, J.-J. Shim, S. Parida, in: Sulfur doping: unique strategy to improve the supercapacitive performance of carbon nano-onions 11 (8), 2019, pp. 8040–8050.
- [55] H. Wei, H. Wang, A. Li, H. Li, D. Cui, M. Dong, J. Lin, J. Fan, J. Zhang, H. Hou, Y. Shi, D. Zhou, Z. Guo, in: Advanced porous hierarchical activated carbon derived from agricultural wastes toward high performance supercapacitors 820, 2020, p. 153111.
- [56] W. Chen, X. Wang, C. Liu, M. Luo, P. Yang, X. Zhou, in: Rapid single-step synthesis of porous carbon from an agricultural waste for energy storage application 102, 2020, pp. 330–339.
- [57] Z. Zhang, J. He, X. Tang, Y. Wang, B. Yang, K. Wang, D. Zhang, in: Supercapacitors based on a nitrogen doped hierarchical porous carbon fabricated by self-activation of biomass: excellent rate capability and cycle stability 29 (6), 2019, pp. 585–594.
- [58] S. Liu, X. Hu, J. Ma, M. Li, H. Lin, S. Han, in: N/P Codoped Carbon Materials with an Ultrahigh Specific Surface Area and Hierarchical Porous Structure Derived from Durian Peel for High-Performance Supercapacitors 34 (11), 2020, pp. 14948–14957.
- [59] J. Li, F. Luo, T. Lin, J. Yang, S. Yang, D. He, D. Xiao, W. Liu, in: Pomelo peel-based N,O-codoped hierarchical porous carbon material for supercapacitor application 753, 2020, p. 137597.
- [60] N. Cai, H. Cheng, H. Jin, H. Liu, P. Zhang, M. Wang, in: Porous carbon derived from cashew nut husk biomass waste for high-performance supercapacitors 861, 2020, p. 113933.
- [61] P. Ukkakimapan, V. Sattayarat, T. Wanchaem, V. Yordsri, M. Phonyiem, S. Ichikawa, M. Obata, M. Fujishige, K. Takeuchi, W. Wongwiriyapan, M. Endo, in: Preparation of activated carbon via acidic dehydration of durian husk for supercapacitor applications 107, 2020, p. 107906.
- [62] X. Liu, Y. Wen, X. Chen, A. Dymerska, R. Wróbel, J. Zhu, X. Wen, Z. Liu, E. Mijowska, in: One-step synergistic effect to produce two-dimensional N-doped

- hierarchical porous carbon nanosheets for high-performance flexible supercapacitors 3 (9), 2020, pp. 8562–8572.
- [63] H. Wu, W. Yuan, Y. Zhao, D. Han, X. Yuan, L. Cheng, in: B, N-dual doped sisal-based multiscale porous carbon for high-rate supercapacitors 9 (3), 2019, pp. 1476–1486.
- [64] V.S. Bhat, S.G. Krishnan, T.J. Jayeoye, T. Rujiralai, U. Sirimahachai, R. Viswanatha, M. Khalid, G. Hegde, in: Self-activated 'green' carbon nanoparticles for symmetric solid-state supercapacitors 56 (23), 2021, pp. 13271–13290.
- [65] W. Chen, H. Wang, W. Lan, D. Li, A. Zhang, C. Liu, in: Construction of sugarcane bagasse-derived porous and flexible carbon nanofibers by electrospinning for supercapacitors 170, 2021, p. 113700.
- [66] S. Alipoori, S. Mazinani, S.H. Aboutalebi, F. Sharif, in: Review of PVA-based gel polymer electrolytes in flexible solid-state supercapacitors: Opportunities and challenges 27, 2020, p. 101072.
- [67] V. Goodship, D. Jacobs, Polyvinyl Alcohol: Materials, Processing and Applications 16, Smithers Rapra Technology, 2009.
- [68] E. Elaiyappillai, R. Srinivasan, Y. Johnbosco, P. Devakumar, K. Murugesan, K. Kesavan, P.M. Johnson, in: Low cost activated carbon derived from Cucumis melo fruit peel for electrochemical supercapacitor application 486, 2019, pp. 527–538.
- [69] L. Peng, Y. Liang, J. Huang, L. Xing, H. Hu, Y. Xiao, H. Dong, Y. Liu, M. Zheng, in: Mixed-biomass wastes derived hierarchically porous carbons for high-performance electrochemical energy storage 7 (12), 2019, pp. 10393–10402.
- [70] L. Liu, S. Hu, K. Gao, in: Cellulose Nanofiber Based Flexible N-doped Carbon Mesh for Energy Storage Electrode With Super Folding Endurance 17, 2020, p. 100441.
- [71] Q. Niu, Q. Tang, X. Sun, L. Wang, K. Gao, in: Wood-based carbon tubes with low-tortuosity and open tubular structure for energy storage application 57 (8), 2022, pp. 5154–5166.
- [72] L. Li, Q. Zhong, N.D. Kim, G. Ruan, Y. Yang, C. Gao, H. Fei, Y. Li, Y. Ji, J.M. Tour, in: Nitrogen-doped Carbonized Cotton for Highly Flexible Supercapacitors 105, 2016, pp. 260–267.
- [73] D. He, L. Wu, Y. Yao, J. Zhang, Z.-H. Huang, M.-X. Wang, in: A Facile Route to High Nitrogen-containing Porous Carbon Fiber Sheets From Biomass-flax for High-performance Flexible Supercapacitors 507, 2020, p. 145108.