Research progress on nitrogen doping modification of biomass activated carbon materials for supercapacitors

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Abstract. Supercapacitors have attracted much attention in the field of energy storage due to their high specific capacitance, stable cycle efficiency, and efficient charging and discharging capabilities. The selection of electrode materials can affect the overall performance of supercapacitors. Biomass, as a new type of raw material, is widely used as a precursor for carbon in supercapacitors due to its abundant sources, unique physical structure, and low manufacturing costs. This not only increases the utilization value of biomass, but also reduces the use of non renewable resources. However, biomass derived carbon materials themselves have limited specific surface area, irregular and underdeveloped pore structure, and relatively fragile spatial structure. Nitrogen doping is a common modification method for biomass carbon materials. This article takes various biomass derived carbon materials as research objects, using potassium hydroxide as an activator and nitrogen atom doping method for modification, to prepare supercapacitor electrode materials with unique physical morphology and excellent electrochemical performance.

Keywords: Supercapacitor, Electrode material, Biomass, Activation, Nitrogen-doped.

1. Introduction

With the development of society and the advancement of technology, the energy sector has become increasingly critical resource allocation. At the same time, the demand for energy is increasing rapidly, and the burning of a large amount of fossil fuels has caused severe environmental degradation. On the environment, in order to alleviate the serious consequences of this, the development of renewable energy solutions has become imperative. Especially in the field of energy storage, the research and development of new technologies for efficient energy conversion and storage has become one of the effective paths to address the energy crisis while adhering to sustainable development.

Supercapacitor research and development plays a crucial role in energy storage due to its exceptional characteristics including high specific capacitance, superior power density, and rapid charging capability. Consequently, continuous innovation in electrode materials is essential to maintain outstanding performance in electrical energy storage systems.Supercapacitors primarily store energy through two mechanisms: electric double-layer capacitance and faradaic pseudocapacitance. Structurally, they consist of two electrodes immersed in electrolyte. When an external power source is connected to the supercapacitor, the positive electrode attracts anions while the negative electrode attracts cations, inducing ion migration within the electrolyte and charge separation at the electrode-electrolyte interfaces. This ion accumulation at the electrode surfaces generates an electric double layer that stores electrical energy. The electrode material is a critical component determining overall performance. Both chemical activation (using activating agents) and atomic doping can significantly enhance the electrochemical properties of electrode materials. Activated carbon has been widely adopted as an electrode material in supercapacitors owing to its abundant sources and excellent stability. Concurrently, biomass materials have emerged as highly promising carbon precursors due to their low cost, inherent heteroatom content, and facile extraction processes. These advantages make biomass-derived materials ideal natural carbon sources for supercapacitor applications. An optimized pore structure is essential for achieving high conductivity. This study focuses on biomass materials including reed straw and yuzu peels. Potassium hydroxide activation enables controlled pore formation while preserving the structural integrity of the material,

thereby enhancing its conductive properties. Furthermore, nitrogen doping can significantly enhance material properties through multiple mechanisms: improving electrode wettability, facilitating Faradaic reactions and providing additional pseudocapacitance. This modification strategy is particularly effective because nitrogen and carbon have similar atomic radii, enabling facile substitution of carbon atoms in the lattice structure. The higher electronegativity of nitrogen induces charge redistribution, increasing the charge density of adjacent carbon atoms in nitrogen-doped materials. These synergistic effects collectively contribute to superior electrochemical performance and substantially improved supercapacitor characteristics.

2. Preparation Method

2.1. In-situ nitrogen doping method

By directly using precursors containing both carbon (C) and nitrogen (N) (such as melamine, ethylenediaminetetraacetic acid (EDTA), melamine, etc.), pyrolysis was carried out in an inert gas environment to directly embed nitrogen atoms into the carbon matrix.

2.2. Post treatment nitrogen doping

Prepare carbon materials first, and then mix them with nitrogen sources (such as urea, ammonia, etc.) to high-temperature treatment.

3. Biomass materials

3.1. Yuzu peel

As a typical biomass material, yuzu peel primarily consist of polysaccharides and dietary fiber, while being rich in nitrogen-containing organic functional groups. Nitrogen rich waste yuzu can be used as both a carbon source and a nitrogen source to prepare nitrogen doped porous carbon materials through hydrothermal combination and activation. At the same time, potassium hydroxide used as an activator to explore its effect on the morphology and electrochemical properties of carbon materials.

Wu et al. [1] employed yuzu peel as a carbon precursor, and the sample exhibited relatively excellent electrochemical performance when activated with potassium hydroxide as an activator under nitrogen protection and calcined at 800°C. They named it SPC-800. For comparative analysis, they prepared two control samples: (1) SPC - without any chemical activation and (2) SPCH-800 - activated with phosphoric acid solution instead of KOH, while maintaining identical other preparation conditions. The morphology of biomass derived carbon materials was characterized using Scanning Electron Microscope (SEM), shown in Fig 1. It can be seen from Fig 1 that after potassium hydroxide treatment, a large number of pores were generated due to its etching effect, resulting in a significant increase in specific surface area of 1174.39 m^2/g. The average pore size of the micropores was 1.96 nm, indicating that potassium hydroxide activation mainly generates a large number of micropores within the carbon framework [2]. Micro pores provided a larger contact area between the electrode and electrolyte, significantly increasing the specific capacitance of carbon materials [3].

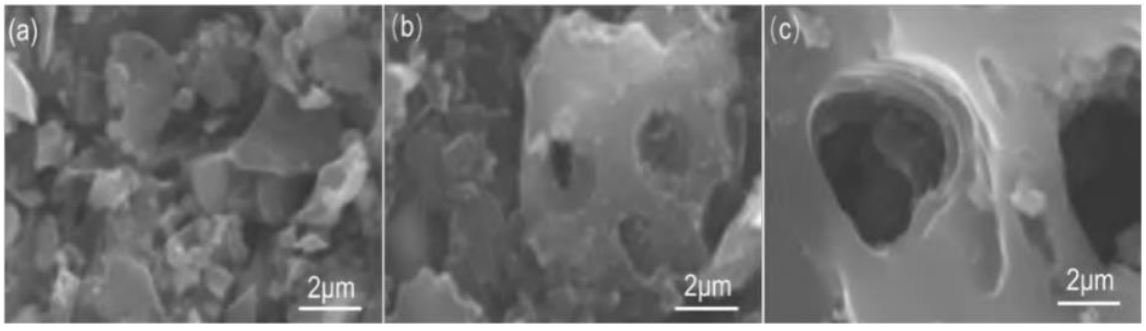


Fig. 1 SEM image of SPC (a), SPCH-800 (b) and SPC-800 (c)

Observation using X-ray photoelectron spectroscopy (XPS) technology revealed the presence of nitrogen atoms in the activated product, indicating the self-doping of nitrogen atoms in grapefruit peel derived carbon materials. At the same time, it was found that the Cyclic Voltammetry (CV) curve showed in Fig 2 (a) still maintained a quasi-rectangular shape under high scanning speed conditions, indicating that it is mainly a double-layer charge energy storage [4]. The CV curve with a scanning speed of 20 mV/S calculated that the electrode material SPC-800 has a specific capacitance of approximately 175.4 F/g at a current density of 1 A/g. Fig 2 (c) showed the curve of capacitance density versus capacitance effect of the three products. The Spc-800 has the highest specific capacitance under all current densities. Fig 2 (b) showed the Galvanostatic Charge-Discharge (GCD) curves of the three products at a current density of 1 a/g. It can be seen that the image shapes of all materials are roughly symmetrical isosceles like triangles, indicating that the energy storage mode is the coexistence of electric double layers and pseudo capacitors. It was consistent with the CV Curve and the calculated diffusion contribution and capacitance contribution, as shown in Fig 2 (e). The Electrochemical Impedance Spectroscopy (EIS) diagram shown in Fig 2 (d) intuitively reflected that the ion diffusion resistance is low and the ion diffusion performance is good. The outstanding performance was attributed to its high nitrogen doping and rich pore structure. The high nitrogen doping amount resulted in good wetting performance of the pores [5], and the rich pore structure enhanced ion transport performance, high transport efficiency, and reduced resistance during charge transfer. Finally, to further validated its performance, cyclic stability tests were conducted, and it was found that it had a specific capacitance of 140.67 F/g after 5000 cycles of discharge, with a capacitance retention rate of up to 96%, shown in Fig 2 (f).

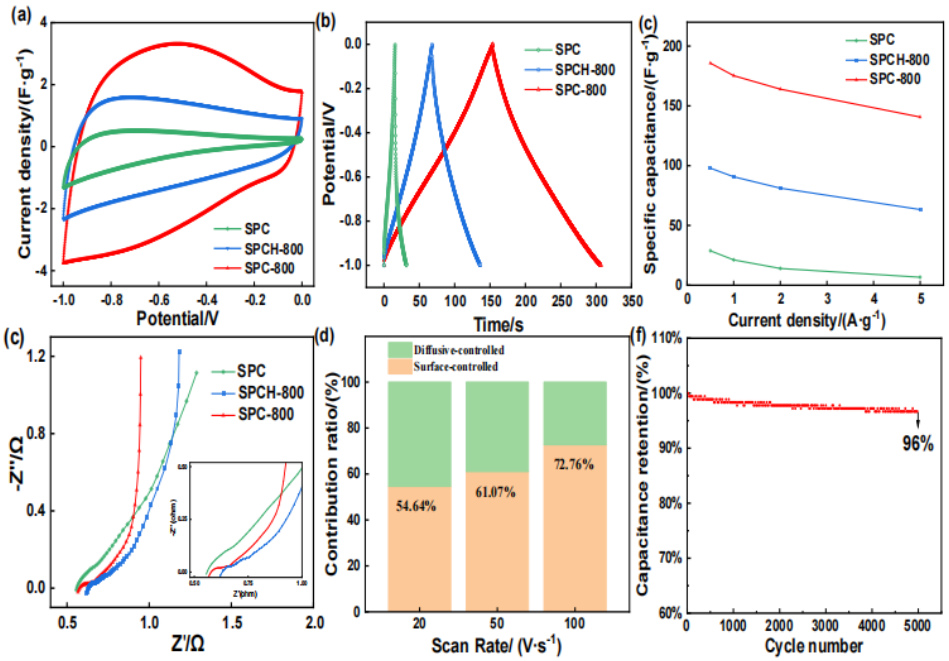


Fig. 2 CV (a), GCD (b), current density effect curve on specific capacitance (c) of SPC, SPCH-800, and SPC-800, EIS (d), Surface capacitance and diffusion capacitance contribution rate of SPC-800 at different scan speeds (e), Cycle capacitance retention curve (f)

3.2. Corn cob

Corn cob, as a type of agricultural waste, was selected as a raw material for preparing carbon-based materials for supercapacitors. This approach not only reduces the manufacturing cost of supercapacitors but also mitigates environmental pollution caused by harmful gas emissions from the large-scale combustion of agricultural waste. Nitrogen doped biomass based porous carbon was prepared by mixing trichlorocyanamide, biochar, and potassium hydroxide from corn cob using a two-step method of pre carbonization and chemical activation. The effects of this method on the morphology and surface chemical composition of the resulting material were investigated.

Chou Lele et al. [6] utilized corn cob as a carbon precursor, maintaining a mass ratio of 1:3 between biochar and potassium hydroxide. The resulting porous carbon material exhibited the best performance at a nitrogen source and biomass content of 1:1 and an activation temperature of 800 °C and was named as MAC1-800. When other conditions remain unchanged, only the ratio of nitrogen source to biomass content is changed. When the mass ratio is 0.5:1, it was formerly named as MAC0.5-800, and when the mass ratio is 2:1, it was formerly named MAC2-800 both as the control group. Fig 3 showed the SEM images of the three samples. From the SEM image and SEM-Energy Dispersive X-ray Spectroscopy (EDS) elemental distribution map, it can be seen that when the mass ratio is 1:1, a honeycomb structure that can serve as a storage site and transport channel for charged ions forms in the sample due to the overflow of biochar and melamine decomposition products during high-temperature pyrolysis, as well as their etching effect on the carbon matrix [7]. The sample primarily consists of carbon, but nitrogen and oxygen were also detected in the EDS mapping, confirming successful nitrogen doping into the corn cob-derived porous carbon. The amount of melamine added significantly influences the material's performance. Moderate melamine addition enhanced the specific surface area and facilitated efficient energy storage. Under these optimized conditions, the processed material exhibits the best hierarchical pore structure, where mesopores and macropores can provide fast transport channels for ions and electrons to micropores, improving capacitor conductivity. While micropores provided a large interface area for charge storage reactions [8].

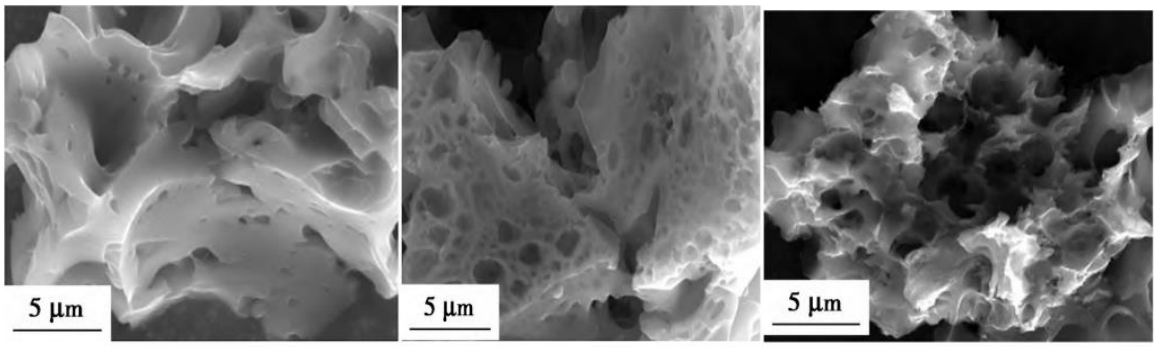


Fig. 3 SEM image of MAC0.5-800 (a), MAC1-800 (b) and MAC2-800 (c)

The processed material was tested in a three electrode system and the CV curve was observed at a scan rate of 10 mV/s. It had the largest coverage area and exhibited the highest capacitance compared to other different processing methods. To explore the practical application value of MAC in supercapacitor electrode materials, it was assembled into symmetrical supercapacitors. As the scanning rate increased, the CV curve always maintained mirror symmetry, indicating that the prepared electrode has good reversibility. At the same time, the area enclosed by the CV curve gradually expanded and deviated slightly from the rectangle, but the degree of deviation was not significant, exhibiting typical double-layer capacitance behavior [9]. Finally, according to the GCD curve calculation, when the current density was 0.5 A/g, the specific capacitance was 233 F/g, and the capacitance retention rate reached 83.3%. After 10000 cycles, the capacitance retention rate reached 82.2%.

3.3. Reed straw

Reed straw, as a natural biomass material, has many uniform hollow possesses numerous uniform hollow tubular structures, and the gaps between the upper and lower layers of the wall facilitate the rapid movement of charges. Using reed straw as a biomass carbon source, which have a natural plant fiber-like structure, has unique advantages in preparing supercapacitor electrode materials. The preparation method adopts the in-situ synthesis method, through the synergistic effect of potassium hydroxide and melamine, the influence of changing the melamine content (nitrogen doping ratio) on the morphology and properties of the material was explored.

Hu [10] employed reed straw as a carbon precursor, and named it N-RSPC-1 when 0.3 g melamine was added. This treatment enabled the material to retain the natural hollow structure of the reed straw while developing more uniform surface pore structures. These modifications increased the contact area between the material and the electrolyte, alleviated the volume effect during charge/discharge, and improving the performance of supercapacitors. However, when excessive melamine was added, the synergistic effect between the two becomes a burden, reducing its specific surface area and lowering its electrochemical performance. Further investigated the specific surface area and pore distribution characteristics of the prepared material through nitrogen adsorption desorption curves. Under otherwise identical conditions, the group without nitrogen doping reaction was called RSPC. When the amount of melamine added was 0.15, it was formerly named as N-RSPC-0.5. When the amount of melamine added was 0.45, it was formerly named N-RSPC-1.5 as the control group. Fig 4 (a-e) displayed the SEM images of the three samples. As shown in Fig 4 (f-h), it can be clearly observed that when the nitrogen doping ratio was 1:1, the sample retained the intrinsic hollow tubular structure of reed straw while exhibiting numerous porous structures on its surface. Further observation through high-resolution transmission electron microscope (TEM) images revealed clear and disordered lattice stripes, which was a typical feature of amorphous porous carbon due to the synergistic effect of melamine and potassium hydroxide at high temperatures. The observed wide lattice spacing facilitated enhanced electrolyte ion transfer and diffusion within the active material, thereby improving the supercapacitor's electrochemical performance [11].

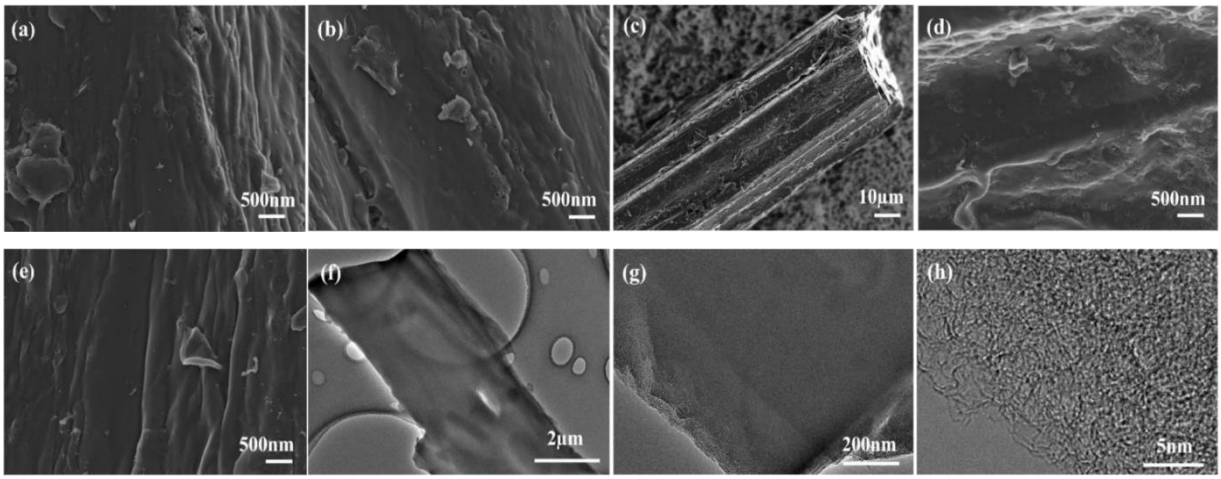


Fig. 4 SEM image of RSPC (a), N-RSPC-0.5 (b), N-RSPC-1 (c) (d), N-RSPC-1.5 (e) and TEM image of N-RSPC-1 (f-h)

Simultaneously, under the condition of a nitrogen doping ratio of 1:1, the specific surface area of the material reached its maximum (1929 m^2/g), which was attributed to the addition of melamine increasing the pore structure of the material. But as the nitrogen doping ratio increases, the specific surface area of the material begins to decrease. Based on this, a pore distribution curve was also drawn, and the results showed that the material under this condition had the highest absorption peak at 1-100 nm, indicating that nitrogen doping in biomass derived carbon materials can significantly increase pore volume. According to the GCD curve, the specific capacity of the material at a current density of 1 A/g is calculated to be 292 F/g, with a capacitance retention rate of 68%. In order to further explore the potential application of electrode materials under this condition, a button type symmetrical supercapacitor was fabricated for experimentation. Fig 5 (a) and (b) showed the CV Curve of N-RSPC-1 electrode material at the scanning speed of 5-100 mV/s and the GCD curve at the current density of 0.5~10 A/g under two electrodes, respectively. The CV Curve showed a distorted shuttle shape, indicating that it has not only the electric double layer storage mechanism but also the pseudocapacitance storage mechanism. At the same time, the GCD curve is approximately isosceles triangle, indicating that the supercapacitor has outstanding electric double layer capacitance characteristics. At a current density of 1 A/g, the specific capacitance of the N-RSPC-1 electrode material was measured to be 90.4 F/g. Based on the Ragone plot shown in Fig 5 (c), the maximum

energy density and power density reached 6.3 Wh/kg and 5000 W/kg, respectively. After 10000 charge-discharge cycles at a current density of 3 A/g, the capacitance retention rate was 92% shown in Fig 5 (d), indicating good cycling stability.

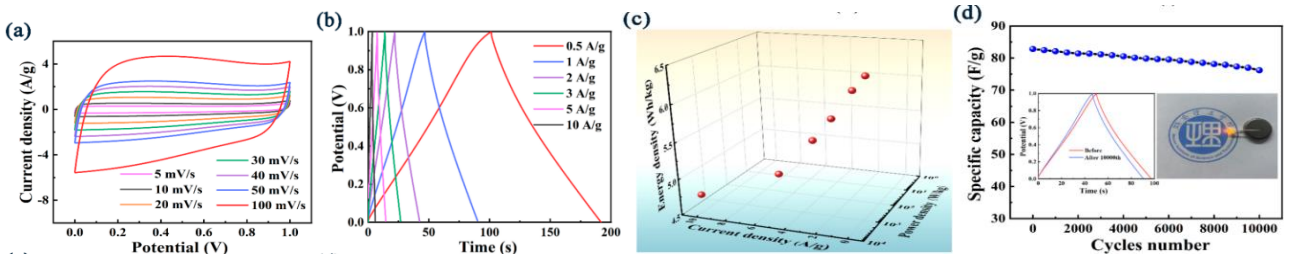


Fig. 5 CV curve at scan rates of 5-100 mV/s (a), GCD curve of N-RSPC-1/N-RSPC 0.5-10A/g (b), Ragone plot at different current densities (c) and Cycle stability curve of electrode materials at 3 A/g (d)

3.4. Sorghum distiller's grains

Sorghum distiller's grains, as a by-product of production, contain abundant nutrients with a crude protein content of about 22% and other amino acids, indicating their high carbon content. Using potassium hydroxide as an activator and melamine as a dopant, an innovative dry ball milling technique was employed to uniformly mix the three. Through pretreatment carbonization and activation, a hierarchical porous carbon material derived from distiller's grains was prepared, and the effects of different doping ratios on the structure and electrochemical properties were explored.

Xu [12] investigated sorghum distiller's grains as a carbon precursor in their experimental study. Through SEM and TEM observations revealed that when the mass ratio of carbon precursor to potassium hydroxide to melamine was maintained at 1:3:1, the sample (designated NVPC-1) exhibited significantly enhanced surface roughness with distinct edge warping. The nitrogen doping induced pore expansion effect was beneficial for increasing the contact area of the electrolyte, and the overall electrochemical performance was the best. For comparative analysis, control samples were prepared under identical conditions, when the ratio of the three is 1:3:0, it was formerly named as NVPC-0, and when the ratio was 1:3:2, it was formerly named NVPC-2 as the control group, with NVPC-1 as the main research object. After elemental scanning analysis, successful doping of N atoms and uniform distribution on the material surface were beneficial for improving the specific capacity of the sample. In further analysis of the sample structure, the pore structure and pore size distribution of the electrode material were characterized. The average pore size of the material was measured to be 2.40 nm, and its specific surface area was calculated to be 3442.97 m^2/g. Compared with the average pore size of 1.8 nm in the undoped nitrogen material, the specific surface area of 2450.82 m^2/g further indicates that nitrogen doping promotes pore growth. The formation of rich pore structures in the framework was related to the decomposition of unstable components during carbonization, which generated gaseous byproducts (such as CO, NO, etc.) [13]. Based on the excellent microporous structure, sufficient active sites can be provided to store charges, and the more charges stored, the larger the specific capacitance [14, 15]. These characteristics are illustrated in Fig 6.

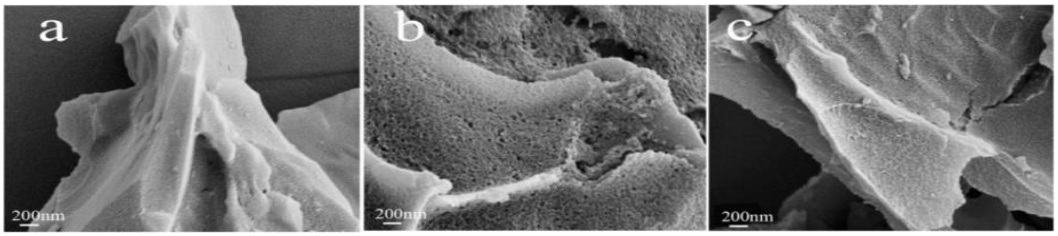


Fig. 6 Scanning Electron Microscopy of NVPC-0 (a), NVPC-1 (b) and NVPC-2 (c)

Subsequently, the wettability of the sample was tested by the contact angle of water droplets, as shown in Fig 7. When the water droplets were on the surface of the doped material, they were fully

absorbed within 13 seconds in the nitrogen doped sample, indicating that nitrogen-doping improved the wettability of the material.

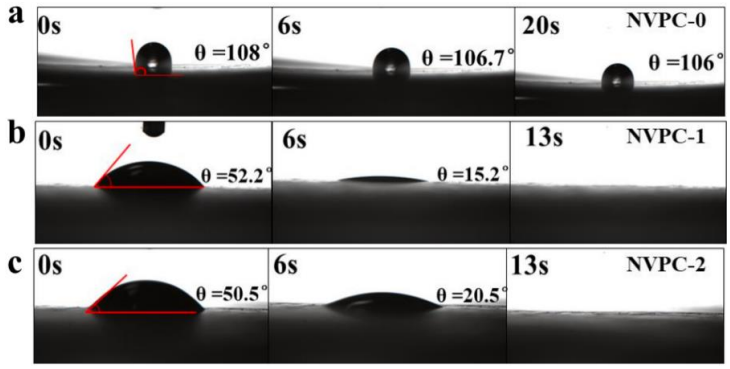


Fig. 7 The variation of water droplet contact angle with time for different samples

Additionally, observe the CV curve of the sample at a scanning rate of 20 mV/s. Compared to materials without nitrogen doping, it exhibited a larger surrounding area and exhibits the best specific capacity. In the GCD test with a current density of 1 A/g, the GCD curve was nonlinear and nearly symmetrical, indicating both double-layer capacitance and pseudocapacitance behavior, as well as a good Coulombic efficiency during charge-discharge cycles. The specific capacity reached 413 F/g at 1 A/g current density. As the scanning rate increases, the CV curve maintained a capacitance performance similar to a rectangular shape, indicating excellent capacity retention and reversibility of the sample. Finally, the cyclic stability of the sample was tested. In the three electrode electrochemical test, even after 10000 cycles at a high current density of 50 A/g, the sample capacity retention rate was 107% and the coulombic efficiency was 100%, These results are illustrated in the Fig 8.

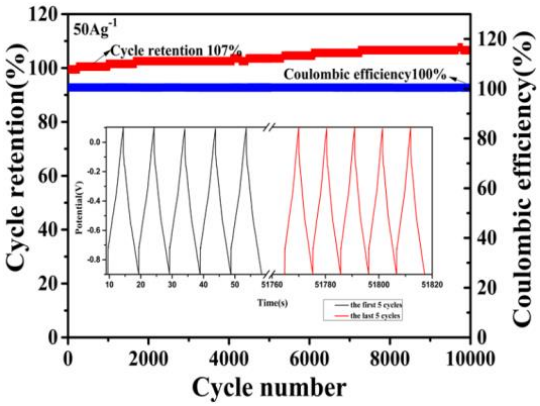


Fig. 8 Cycle stability plot of NVPC-1 in potassium hydroxide alkaline electrolyte at a current density of 50 A/g, with the middle inset showing the GCD curves for the first 5 cycles and the last 5 cycles

3.5. Cotton Tree

Cotton fiber is currently the lightest, thinnest, and most hollow fiber material in the world. It uses chitosan as a binder, potassium hydroxide as an activator, and urea solution as a nitrogen source introduction agent to evenly distribute it on the outer wall of the cotton fiber pipeline and the surface of the layered structure of chitosan. After freeze-drying and high-temperature carbonization, nitrogen doped kapok based carbon aerogel with high porosity was obtained, and its electrochemical performance was systematically investigated.

Zhang [16] employed cotton as a carbon precursor. The structural characteristics of the material were observed by SEM, TEM and EDS. The sheet-like structure of the material was closely interconnected with the tubular structure, interweaving with each other to form a complete three-dimensional network structure. The interior maintained a hollow state, which preserved ion transport

channels. Higher-magnification SEM images revealed that the sample's pore structure consisted of numerous micropores Fig 9 (a-f), providing a high specific surface area and facilitating ion diffusion [17]. After high-temperature carbonization at 900 °C, the material exhibited higher porosity (73.5%) compared to other temperatures, which could provide more ion adsorption sites and improve the overall electrochemical performance of the sample as an electrode material for supercapacitors. This sample under this condition was formerly named as N-CK900. Keeping other conditions constant, the sample with a carbonization temperature of 700 °C was referred to as N-CK700, and the sample with a carbonization temperature of 800 °C was referred to as N-CK800 both as the control group. In the structural characterization of the sample, it was found that the sample material has a high degree of defects, which was beneficial for the wettability of the material and can provide more active sites for ion transport, further improving the electrochemical capacitance of the material [18].

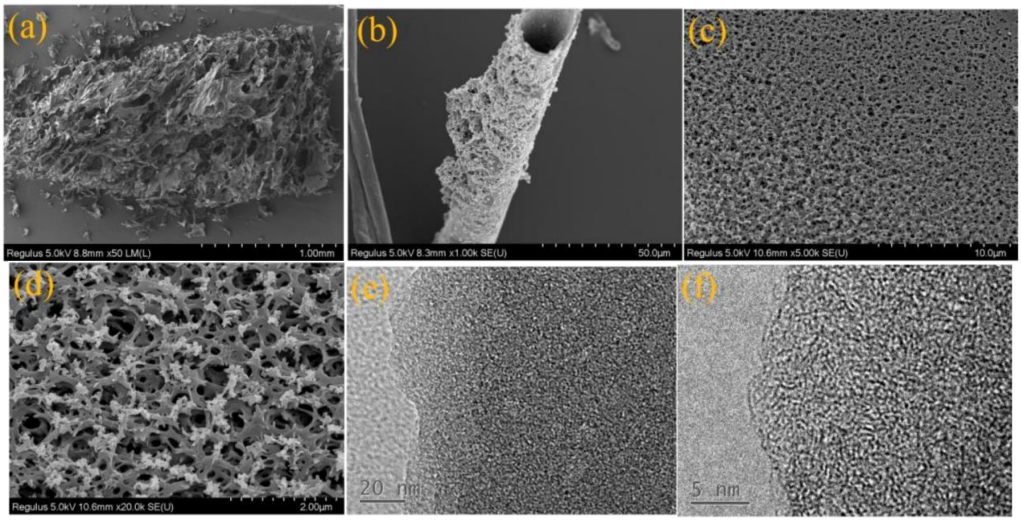
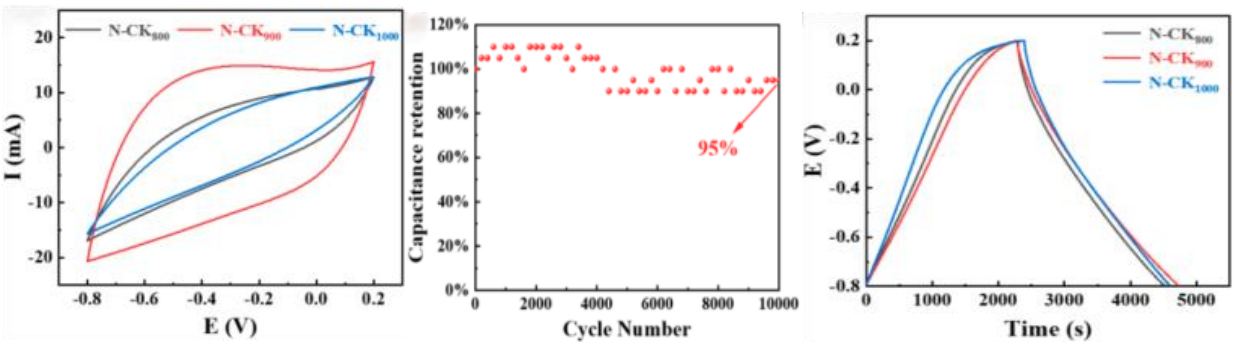


Fig. 9 SEM images of N-CK900 at different scales (a-d) and TEM images of N-CK900 at different scales (e-f)

To better analyze the effect of exogenous nitrogen doping on materials, the CV performance of the material electrode material was tested at a scan rate of 50 mV/s in a three electrode system. The material carbonized at 900 °C exhibited the largest enclosed CV area, optimal capacitance characteristics, and the highest specific capacitance value shown in Fig 10 (a). This may be attributed to the excellent porosity of the composite material during the carbonization process at 900 °C , which was conducive to the diffusion and transport of electrolyte ions [19]. In the GCD tests conducted at 0.1 A/g, the material displayed nearly ideal triangular GCD curves shown in Fig 10 (b), indicating excellent Coulomb efficiency. Subsequently, the capacitance value of the material was calculated to be 246.2 F/g. Furthermore, the sample demonstrated outstanding cycling stability, maintaining 95% of its initial capacitance after 10,000 cycles shown in Fig 10 (c), confirming its excellent long-term electrochemical stability.



(a) (b) (c)

Fig. 10 CV curve at 50 mV/s (a), constant current charge discharge curve at 0.1 A/g (b) and cycle stability image (c)

3.6. Sand Willow

As a unique vegetation in western China, Sand Willow is frequently discarded due to the lack of effective utilization methods. A large amount of Sand Willow branches are pruned every year, resulting in resource waste. By developing Sand Willow activated carbon to prepare supercapacitor materials, the manufacturing cost is reduced while increasing the added value of Sand Willow. Salix matsudana was used as a precursor and potassium hydroxide is used as an activator to prepare Sand Willow activated carbon using a two-step carbonization activation method. At the same time, melamine was introduced as a nitrogen source into Sand Willow activated carbon electrodes to explore the effect of nitrogen doping on the morphology, structure and electrochemical performance of Sand Willow activated carbon electrodes.

Qiu [20] employed Sand Willow as a carbon precursor, when processed at 700 °C with a mass ratio of raw material to melamine of 1:2, the nitrogen-doped material demonstrated optimal electrochemical performance and was designated as SAC-N-2, while keeping other conditions unchanged. The sample without nitrogen doping was named as SAC-700-3, where 3 represented an alkali carbon mass ratio of 3:1, which was the same as the prerequisite for nitrogen doping mentioned above. Under low relative pressure conditions, the sample doped with nitrogen has a higher adsorption capacity, indicating that the introduction of nitrogen source not only increased the number of micropores but also optimized the quality of the pores. By analyzing the pore size distribution map, the sample exhibited strong peaks in the microporous region below 2 nm and the mesoporous region between 2-7 nm, indicating that the sample was mainly composed of micropores and mesopores. By introducing nitrogen atoms to optimize this combination, not only did it increase the material's adsorption capacity, but it may also enhanced its application in energy storage. By further observing the microstructure of the material through SEM images shown in Fig11 (a) and (b) it was found that the surface of the material became rougher and more irregular after nitrogen atom doping, indicating the possible introduction of new active sites and an increase in the number of pores. At the same time, nitrogen atoms were uniformly distributed on the surface of activated carbon, which was beneficial for improving the electrochemical properties of the material. As nitrogen atoms could act as catalytic sites, they promoted electron transfer.

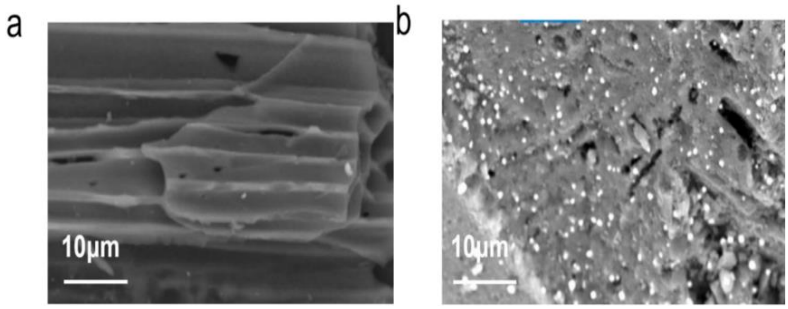


Fig. 11 Electron microscopy image without nitrogen doping (a) and electron microscopy image with nitrogen doping (b)

In the three-electrode system, the CV curve obtained at a scan rate of 20 mV/s exhibited no obvious oxidation-reduction peak in the sample, indicating that its capacitance mainly originated from the double-layer effect rather than pseudocapacitive behavior [21]. At the same time, the CV curve of the sample was closer to the rectangular shape of an ideal capacitor shown in Fig 12 (a), indicating that nitrogen doping effectively enhanced the electrochemical performance of the material by enhancing pseudocapacitance and specific capacitance. In addition, the GCD curve of the material was closer to linearity and symmetry shown in Fig 12 (b), indicating its superior charge discharge performance and electrochemical stability. According to the curve, the specific capacitance of the sample at a current density of 1 A/g was calculated to be 290.1 F/g. Then, the scanning speed was increased to 100 mV/s, and the capacitance contribution accounted for 90.3% of the entire capacitance shown in Fig 13 (b). Through the analysis of the capacitance contribution rate chart shown in Fig 13 (a), it was found that as the scanning rate increased, capacitance dynamics dominate, which was beneficial for improving

the rate characteristics and cycling stability of electrode materials. Finally, the sample was subjected to cyclic stability testing. After 10000 cycles of charging and discharging at a current density of 5 A/g, the capacitance retention rate was 93.2% shown in Fig 13 (c), indicating its excellent cyclic stability performance.

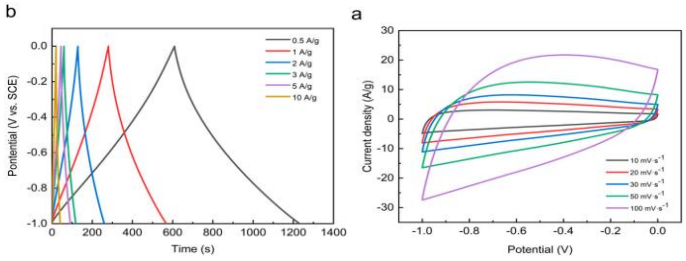


Fig. 12 CV curve of SAC-N-2 (a) and GCD curve of SAC-N-2 (b)

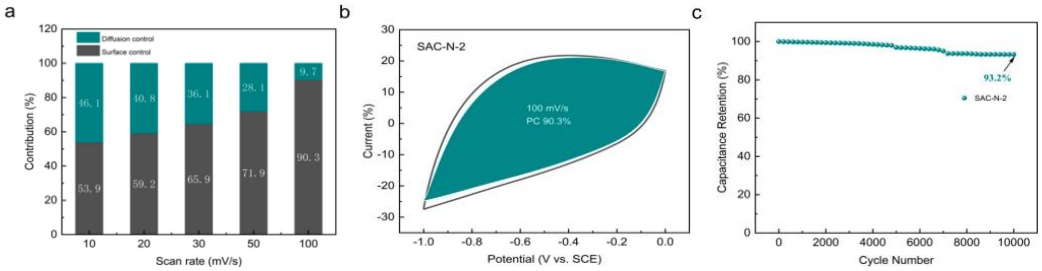


Fig. 13 Contribution rate of capacitance at different scanning rates (a), surface controlled capacitance at a scanning speed of 100 mV/s (b) and cycle stability curve of SAC-N-2 electrode after 10000 charge and discharge cycles (c)

3.7. Celery stems

Celery stem is the stem of herbaceous plants. As the connecting part between the roots and flowers and leaves of herbaceous plants, celery stem plays a role in transporting water and nutrients. It contains a large amount of microtubule tissue and thin-walled cells, making it an ideal carbon material for preparing porous carbon [22, 23]. Due to the large amount of moisture in the raw materials, improper removal may affect the structure of the tissue and thus affect the performance of porous carbon. Vacuum freeze-drying was employed to remove moisture while preserving the original micro pore structure of the tissue, and pre oxidation can be carried out using aerobic baking, and influencing on the structure and properties of porous carbon [24]. Using celery stems as precursors, potassium hydroxide as a green activator, and urea as a nitrogen dopant, various characterization methods were employed to investigate the effect of activation and nitrogen doping conditions on the electrochemical performance of the samples.

Pei [25] used celery stems as carbon precursors. When the aerobic baking temperature is 200 °C and the mass ratio of raw materials to urea is 1:1, the overall electrochemical performance of the material is significantly improved, and it was named as CF200-1. When keeping other conditions constant, change the aerobic baking temperature to 0 °C , 250 °C and 300 °C respectively, denoted as CF000-1, CF250-1, and CF300-1. Comparing the SEM characterization images shown in Fig 14 (a-d) of aerobic baking at 250 °C and unbaked samples, and analyzing the isothermal adsorption desorption curves of the samples, it was found that aerobic baking pretreatment is beneficial for the generation of micropores. With the increase of the back temperature, the number of micropores and nitrogen adsorption capacity of porous carbon increase, but the overall nitrogen adsorption capacity of porous carbon was affected, and the mesoporous structure was destroyed. To further analyze the electrochemical performance of the sample, constant current charge discharge tests were conducted at a current density of 1 A/g to obtain the GCD curve. It was found that the GCD curve of the sample was a regular isosceles triangle, and the high specific capacitance of the sample could be attributed to its good pore structure. The reasonable proportion between mesopores and micropores affected the electron transfer, thereby affecting the energy storage performance of porous carbon. Meanwhile,

aerobic baking pretreatment helped to introduce more nitrogen into the interior of porous carbon, improving its wettability and reducing its equivalent resistance [23].

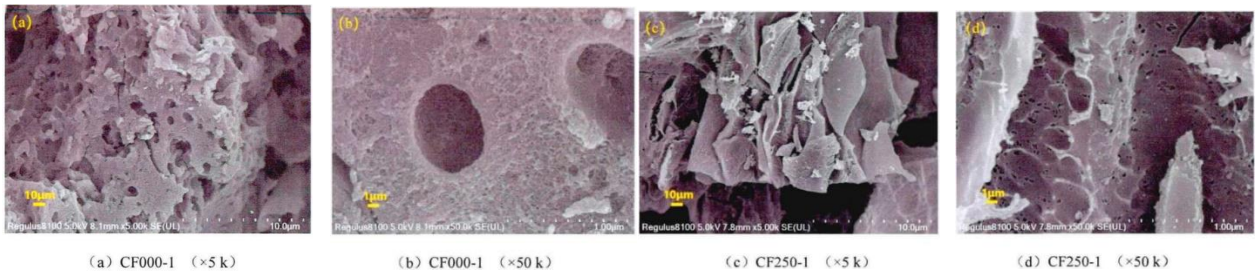


Fig. 14 SEM characterization at different baking temperatures

At an aerobic baking temperature of 200 °C the GCD curve of the sample maintained regular isosceles triangle during the current density variation from 0.5 A/g to 50 A/g, demonstrating the good double-layer capacitance characteristics of the sample. The CV curve of the sample was obtained at a scanning rate of 50 mV/s, and it was found to have good symmetry and a regular rectangular shape, indicating that the capacitance of the sample is mainly provided by the double-layer capacitance. Even at higher scanning rates, the sample still maintained a good rectangular shape, proving that the sample has good power capacity. Then, the specific capacitance variation of the sample was observed at different current densities. When the current density increased from 0.1 A/g to 50 A/g, the specific capacitance retention rate of the sample remained at 71.8%, and the capacitance rate performance was good. Finally, the cyclic stability test of the sample was conducted. At a current density of 5 A/g and 5000 cycles, the capacitance retention rate reached 96.2%. This may be due to the improvement of the pore structure of the sample during aerobic baking treatment, which strengthened the nitrogen doping effect. Moreover, after 5000 cycles, the GCD curve of the sample maintained a good isosceles triangle, proving the stability of the sample.

4. Conclusion

Using biomass materials as carbon precursors in supercapacitors not only embodies the concept of environmental protection and reduces development costs, but also innovates high-performance capacitor materials using natural structures or special structures, promoting the popularization and commercialization of supercapacitors. Most of the biomass materials selected in this article are agricultural waste or by-products generated after product processing, which have been reprocessed to increase the added value of the products. At the same time, nitrogen atoms were introduced as dopants, which improved the physical characterization and electrochemical performance of the material. However, nitrogen atoms may undergo chemical state transformation or dissolution during the cycling process, leading to capacitance decay. At the same time, most raw materials require high temperature conditions during doping in the production process, which poses safety risks and high costs. How to maintain the long-term stability of supercapacitor operation and the feasibility of industrial production still needs further exploration. In conclusion, with the continuous development of society and the advancement of science and technology, biomass nitrogen doped porous carbon materials may be widely used in various new types of capacitor electrode materials, comprehensively replacing supercapacitor electrode materials that use non renewable resources as carbon precursors, thereby driving innovation in energy storage technology.

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