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Highly Ordered Micropores Activated Carbon from Long Fiber Biomass for High Energy Density Supercapacitors

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The electrochemical performance of carbon based supercapacitors not only depends on the specific surface area and conductivity, but also the structure of materials. In order to construct the carbon materials with effective structure, the long fibrous plant-saussurea involucrata stalk was chosen as the new style carbon source. Highly ordered micropores activated carbon (HOMAC) materials have been successfully obtained via KOH chemical activation method. The synthesized HOMAC exhibits high specific surface area of $2692 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $1.14 \text{ cm}^3 \text{ g}^{-1}$. The assembled HOMAC-based electrode can deliver a high specific capacitance of 379 F g^{-1} at 2 mVs^{-1} in $1 \text{ M H}_2\text{SO}_4$ aqueous electrolyte, and show excellent cyclic stability (the capacitance retention $\sim 95\%$) over 10000 cycles at a current density of 1 A g^{-1} , which authenticates excellent charge storage capacity of electrode material. Moreover, the operation voltage window can be expanded to 0–

1.8 V in $1 \text{ M Na}_2\text{SO}_4$ electrolyte for the 2-electrode system. The symmetric supercapacitor can deliver a high energy density of 33.91 Wh kg^{-1} at power density of 180.03 W kg^{-1} . These high performances can be ascribed to the high surface area and ordered microporous structures obtained using KOH as activator. We further discussed the relationship between fibrous plants and electrochemical performances of the final activated carbon materials. This present work can provide beneficial guidance for the preparation of high performance activated carbon electrodes from a biomass-based carbon source. Comparing with two different biomass materials, it can be found that the ionic diffusion coefficient of saussurea involucrata is $5.074 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, which is 2.5 times of cotton stalk ($1.547 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$). This phenomenon indicates the different ion transmission rate in different pore structures.

1. Introduction

With an increasing demand of portable electronic products and electrical vehicles, emerging energy storage and conversion devices have become highly desirable.^[1,2] Particularly, many studies have paid close attention to supercapacitors in recent years, because they have higher power and energy densities than lithium ion batteries and traditional capacitors.^[1,3,4] These researches in supercapacitors have mainly focused on the study of electrode materials, such as transition-metals,^[4,5] conducting polymers,^[6,7] carbon materials and their composites.^[8]

Currently, carbon materials are recognized as the best candidate for electrode materials of supercapacitors due to their high electrical conductivity, environmental friendliness, superior chemical stability and extended cycle life.^[9,10,11] In particular, many kinds of biomass based activated carbon

materials have successfully been used in supercapacitor electrodes, e.g. elm seeds,^[12] peanut shells,^[13] ginger,^[14] foxtail grass seeds,^[15] bagasse,^[16] as they meet the current needs of sustainable development.^[17] However, few reports study the structure-activity relationship between primary biomass features and electrochemical performances of the final products.

In our previous studies, the cotton stalks prepared via KOH activation methods shows high electrochemical performance.^[18] In addition, prediction by using machine learning has indicated that the factors affecting the performance of supercapacitors include specific surface area (S_{BET}), pore volume (V_{tot}), resistance (R_s), aspect ratio (r_{LD}) and cellulose ratio (CL (%)). Among these factors, S_{BET} , V_{tot} and R_s are three major variables.^[19,20] We also raised a conclusion that long fibrous plants have many advantages for activated carbon, including high surface area, aspect ratios, excellent mechanics and hydrophilicity.^[19] Based on these, we chose one same genus plants which has long fibrous feature as initial carbon source. On the one hand, using the prediction as an instruction, it can be used in the practical applications. On the other hand, combined with the work about cotton stalk, it can be examined the effect of fibrous plants as precursor on the physicochemical properties and electrochemical performances of the final activated carbon samples. This work can evaluate which long fibrous plants are superior for preparing hierarchical porous carbon materials.

Herein, saussurea involucrata stalk with long fibrous feature was selected as optimized plant material to produce porous carbon for supercapacitors. A simple synthesis strategy was employed to develop the highly ordered micropores activated

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carbon (HOMAC) material based on *saussurea involucrata* stalk (Scheme 1). Therefore, by measuring these three properties of *saussurea involucrata* stalk-based porous carbons, the prediction which put forward before was reconfirmed. The intrinsic regular relationship between the structure and electrochemical performance was further revealed. This research will provide a valuable reference for the design and fabrication of low cost and high-performance biomass-based hierarchical porous carbon for energy storage. At the same time, the relationship between structure of activated carbon material and ion transmission rate has been mainly explored by a proton transport experiment, which provides a new path for people to select reliable biomass source conveniently for next-generation energy storage devices.

2. Results and discussion

The long fibrous plants usually have natural channels for nutrient transportation. These fibrous bundles could facilitate the absorption of KOH during soaking process. As shown in Figure S2A, the raw material has fibrous structure and smooth surface with few pores. After carbonization, the carbide inherits the specific fibrous structure (Figure S2B). The carbon wall experienced some shrinkage. Some wrinkles appeared on the surface. Some tiny cracks and circular pores are generated, which makes it easier for activator to take effect deep into the internal of the materials and create more pores.

As shown in Figure S3, the typical SEM image of HOMAC-0 significantly deviate from that of the others. HOMAC-0 mainly composed of large wrinkled flakes without porous features (Figure S3 (k, l)). However, after adding the KOH, porous structure with abundant interconnected macropores and mesopores can be observed (Figure S3 (a–j)). This demonstrates KOH could etch carbon framework and bring various pores. Due to the expansion of carbon lattices, HOMAC-2 to 6 samples developed open and deep channels with ordered and continuous pores in hard carbon walls during the activation (Figure S3 (a–j)). For HOMAC-2, less KOH made poor development of porous structure (Figure S3 (a, b)). HOMAC-3 shows interconnected hierarchical porous structure. It can be clearly seen that HOMAC-3 has the uniform arrange ordered pore structure on the carbon particle surface in Figure S4. Due to the expansion of the carbon lattices during the activation, HOMAC-3 exhibits porous graphene-like sheets and more obvious stripping effect (Figure 1 (a, b)).^[18,21,22] These carbon sheets are extremely thin (126–141 nm in thickness), which can be attributed to the

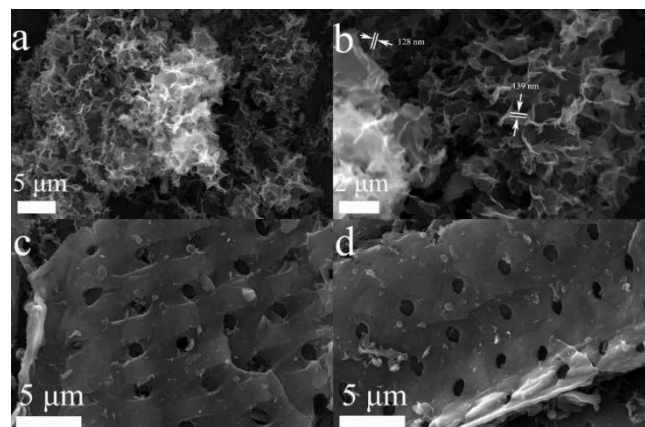
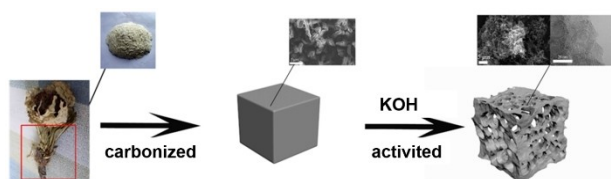


Figure 1. The representative SEM images with different magnification. (a) (b) HOMAC-3. (c) (d) Cotton stalk-based activated carbon materials.^[18]

increased degree of graphitization of activated carbon after adding KOH.^[23]

As for HOMAC-4, 5 and 6 in Figure S3 (e–j), the carbon wall became thinner and 3D skeleton gradually collapsed with the increasing KOH. Some small holes merged to form macropores (Figure S3 (g, i)). More disordered fragments were created. Especially for HOMAC-5 and HOMAC-6, some fine chips fall into holes of the carbon and covered some channels and pores, thus hindering the transferring of electron and the ion transmission (Figure S3j). Compared with other samples, HOMAC-3 exhibits uniform ordered macropores with numerous meso- and micropores on the graphene-like carbon layers, which is favoured for the improvement of electrochemical performance.^[24,25]

Figure 2 and Figure S5 show TEM micrograph of HOMAC, further presenting the porous and ultrathin stacked layers morphology. Figure S5B shows wormhole-like pore structures, which indicates good pore regularity. There are abundant and dense micropores and mesopores on the surface of HOMAC (marked as dotted circles in Figure 2). According to Figure 2(A, B), ordered macropores were distributed uniformly on the graphene-like layers. Figure 2B shows layers of graphene-like sheets with 2-D hexagonal symmetrical pore structure. This multilayer lamellar morphology with well-arranged pore passage presumably due to the etching of KOH. Figure 2C further reveals a wide range of ordered graphite fringes and hexagonal array pore structures.^[26] The graphitized monolith has highly ordered hexagon porous network morphology and obvious



Scheme 1. Schematic diagram of highly ordered micropores activated carbon.

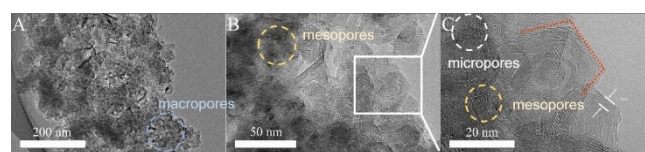


Figure 2. The representative TEM images of HOMAC-3 sample at different magnifications.

graphite stripes (Figure 2C). The six lattice fringes with a distance of 2.18 nm indicates the existence of short-range order carbon structure (Figure 2C). This corresponds well with the (002) plane of graphite (one lattice fringe with a distance of 0.34 nm).^[27] Such clear lattice fringes suggested a good crystallization and highly ordered porous structure.^[21] Ordered lattice arrangement indicates the HOMAC-3 has a few layers graphene, predominantly single-layer carbon, coupled with interconnected regular pores, both can offer a continuous conductive network to increase the conductivity of HOMAC samples and facilitate the ion transport during the fast charge-discharge process.^[28] This result demonstrates that the conjugated sp^2 graphitic domains were successfully constructed in the HOMAC-3.^[29] Additionally, the cotton straw-based carbon also has uniform arranged ordered-pore structure. (Figure 1(c, d))^[18] The structure of long fibrous can be inherited after carbonization and form hierarchical porous structure on the fibrous structure, which has huge potential for charge storage.^[30] It indicates the fibrous structure of the precursor has the potential to form ordered layer-stacked graphene sheets.

X-ray diffraction and Raman characterizations were carried out in order to analyse the intrinsic properties of HOMAC samples. Figure 3A and Figure S6 shows the XRD patterns of the six activated carbon samples. The typical diffraction patterns at approximately 22° and 43° were observed, corresponding to the (002) and (100) plane of graphite, respectively. The broad peaks near 43° indicates that materials have been graphitized. The graphitized carbon atoms were hexagonal planar network structures.^[26,31] A broad peak was observed in HOMAC-0, indicating amorphous carbon structures.^[32] The (002) diffraction peaks are weakened with the increasing KOH, proving an increase in the degree of graphitization and a graphitic crystalline structure was formed.^[11,33] The peak at

$\sim 43^\circ$ denotes the improvement of structural order of HOMAC-3. A significant increase in the peak intensity at low-angle was noticed from HOMAC-3, which indicates the presence of high-density micropores.^[34] In addition, small angle XRD patterns of the HOMAC-3 was recorded in Figure S7 to determine the degree of structural order. HOMAC-3 has clear intense and sharp diffraction peak at around 1.08° , indicating a mesoscopic ordering.^[35,36] This peak corresponds to (100) planes of the 2D hexagonally ordered mesoporous system.^[35] The activation process increased the proportion of micropores in ordered pores, the carbon materials exhibit highly ordered structures with a hexagonal arrangement.^[37] Therefore, the conductivity, stability and corrosion resistance of the materials were superior to amorphous carbon materials.^[26]

The Raman spectrum reinforced these results by showing the two typical carbon characteristic peaks appeared at $\sim 1360\text{ cm}^{-1}$ (D band) and $\sim 1586\text{ cm}^{-1}$ (G band) as shown in Figure 3B. While D band with a double-resonance represents the degree of disorder or structural defects, G band corresponding to graphite in-plane vibrations represents ordered carbon structure.^[38,39] The intensity ratio between D and G bands (I_D/I_G) was calculated to reflect the degree of graphitization of these six samples.^[9,20, 40, 41] The degree of graphitization of HOMACs estimated from I_D/I_G ratio were found to be 1.03, 1.01, 0.98, 1.01, 1.01 and 1.00 for HOMAC-0, HOMAC-2, HOMAC-3, HOMAC-4, HOMAC-5 and HOMAC-6, respectively. HOMAC-0 has the highest I_D/I_G value with 1.03. A decrease in I_D/I_G ratio from 1.03 to 0.98 is observed with the addition of KOH, implying enhanced level of defect structures presumably resulted from more armchair graphite edges.^[42] The lowest I_D/I_G value of HOMAC-3 is 0.98, indicating a higher degree of graphitization, which is due to the graphene-like structure generated effectively by KOH activation treatments. As for HOMAC-4, 5 and 6, the increase in the I_D/I_G ratio reveals a decrease in degree of graphitization with concomitant increase in defect sites.^[43] Furthermore, HOMAC-2 to 6 samples also exhibit low intensity of 2D and D+G bands at ~ 2680 and $\sim 2890\text{ cm}^{-1}$ respectively, which attributed to the existence of few-layer and ordered graphene-like carbon structure.^[44] The above results demonstrate that the spectrum is characteristic of graphene-like nanosheets.^[45] Moreover, the obtained HOMAC products with highly ordered graphitic structure is more beneficial for the transmission of ions in the material.^[46]

The porous texture of the five HOMAC samples were characterized by N_2 adsorption-desorption experiments at 77 K as illustrated in Figure 3C. The typical I/IV isotherms indicates that all five samples have considerable porosity and high surface area. Meanwhile, the major adsorption of these samples occurred at relatively low pressure of less than 0.1 P/P_0 , indicating a significant density of micropores.^[47] A small H4 type hysteresis loop shows horizontal parallel adsorption isotherms, which demonstrate there are narrow slits exists between the adsorption and desorption branches (at 0.4–1.0 P/P_0) of HOMAC-3, indicates that the sample has a small amount of mesopores.^[48] Besides, at high pressure ($P/P_0 > 0.9$), the appearance of the obvious tail implies the existence of macropores within the carbon.^[49] Figure 3D shows the pore distribu-

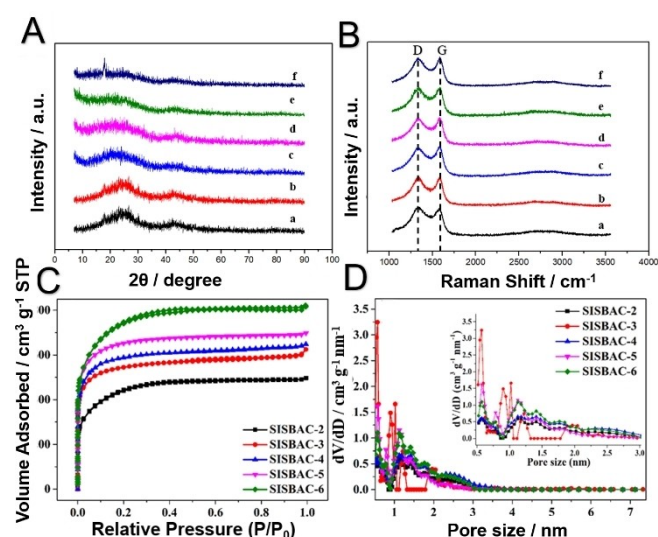


Figure 3. (A) XRD patterns of six samples. (B) Raman spectra of six samples ((a) HOMAC-0, (b) HOMAC-2, (c) HOMAC-3, (d) HOMAC-4, (e) HOMAC-5 and (f) HOMAC-6). (C) Nitrogen adsorption-desorption isotherms of five samples. (D) Pore size distribution of five samples, calculated from the adsorption isotherms using DFT method.

Table 1. The porous textural characteristics of the saussurea involucrata stalk derived carbon materials.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	D_{ave} (nm)
HOMAC-0	34	0.02	2.30
HOMAC-2	1587	0.69	1.74
HOMAC-3	2073	0.89	1.72
HOMAC-4	2255	0.97	1.72
HOMAC-5	2458	1.02	1.66
HOMAC-6	2692	1.14	1.69
FTMAC	1964	1.03	2.09

tions calculated by density functional theory (DFT), which reveals the synthesized porous carbon samples consist of both mesopores and micropores. The pore sizes of micropores and mesopores are in the range of 0.56–1.9 nm and 2.0–3.0 nm, respectively.^[49] The ordered range depends on the pore-width.^[50] Figure 3D shows that HOMAC-3 mainly concentrated in 0.5–1.2 nm of micropores and has sharp strong pore size distribution centered at 0.56 nm. The porosity of HOMAC-3 shows highly developed microporous structure with little mesopores.^[51] Research also shows the effective specific surface area of porous carbon is usually contributed by small pores (0.5–1.1 nm).^[52] HOMAC-2, 4, 5 and 6 mainly concentrated at the sizes of mesopores. The pore size of these samples is listed in Table 1. HOMAC-0 possess the largest average pore size among the samples. This is because HOMAC-0 has no micropores caused by the activation of KOH.

From the prediction, S_{BET} and V_{tot} are two most important features of carbon for the electrodes of supercapacitor.^[19,20] Table 1 provides the porous textural details of six HOMAC samples. HOMAC-0 without KOH activation contains almost no pores and low specific surface area ($0.02 \text{ cm}^3 \text{g}^{-1}$ and $34 \text{ m}^2 \text{g}^{-1}$), and the pore size of 2.3 nm is smaller than other HOMACs. With activation of KOH, the samples exhibit more than 46 times (from 1587 to $2692 \text{ m}^2 \text{g}^{-1}$) enhancement in the specific surface area, at the same time the pore volume increases from 0.69 to $1.03 \text{ cm}^3 \text{g}^{-1}$. This is because the active ions from KOH intercalate with the carbon matrix, widening the space between carbon layers and enhance the total pore volume and surface area. With the usage ratio of KOH increases from 2 to 6, the specific surface area and total pore volume increases from $1587 \text{ m}^2 \text{g}^{-1}$ to $2692.08 \text{ m}^2 \text{g}^{-1}$, $0.69 \text{ cm}^3 \text{g}^{-1}$ to $1.14 \text{ cm}^3 \text{g}^{-1}$ respectively. A large surface area and high pore volume are beneficial for charge storage in pores and fast diffusion of electrolyte at the surface and in the bulk as well, resulting in a better electrochemical property.^[20]

For sustainable practical supercapacitor device operation, the electrode should be tested under ambient conditions, ensuring the environmentally benign aqueous electrolyte at different sweep rates. Therefore, the actual electrochemical performance of HOMACs was examined by CV and GCD measurements in 1 M H_2SO_4 electrolyte with a two-electrode system. Figure S9 and Figure S10 present the gravimetric specific capacitance calculated from the integrated area of CV curves of the five electrodes at different scan rates ranging from 2 mVs^{-1} to 100 mVs^{-1} . The obtained CV curves are rectangular and symmetric in shape from 0 to 1 V. The specific

capacitances of five HOMAC electrodes (HOMAC-2, HOMAC-3, HOMAC-4, HOMAC-5 and HOMAC-6) at the scan rate of 2 mVs^{-1} were 320, 379, 316, 270 and 303 Fg^{-1} , respectively. Notably, the specific capacitance of HOMAC-3 electrode was the highest. Compared with HOMAC-3 to HOMAC-6, less KOH made HOMAC-2 haven insufficient microporous texture, causing less active sites to store charges. The small pore volume of HOMAC-2 also hinders ion diffusion. As for HOMAC-4, 5 and 6, excessive KOH made samples overdeveloped, and the blocked pore tunnels make diffusion path tortuous and lead electrolyte infiltrate difficultly. Besides, HOMAC-3 also retains a specific capacitance of 175 Fg^{-1} at high scan rate of 100 mVs^{-1} (47 % retention). As shown in Figure 4A, HOMAC-3 electrode exhibits an approximately rectangular shape, indicating an ideal electrical double-layer capacitive behaviour. The rectangular CV curve of HOMAC-3 electrode is slightly distorted at a higher scan rate of 100 mVs^{-1} implying low contact resistance in this system. Excellent performance of HOMAC-3 attributed to high specific surface area and optimized porous structure with large volume, which is in accordance with the results of machine learning. In addition, HOMAC-0 possess a really small specific

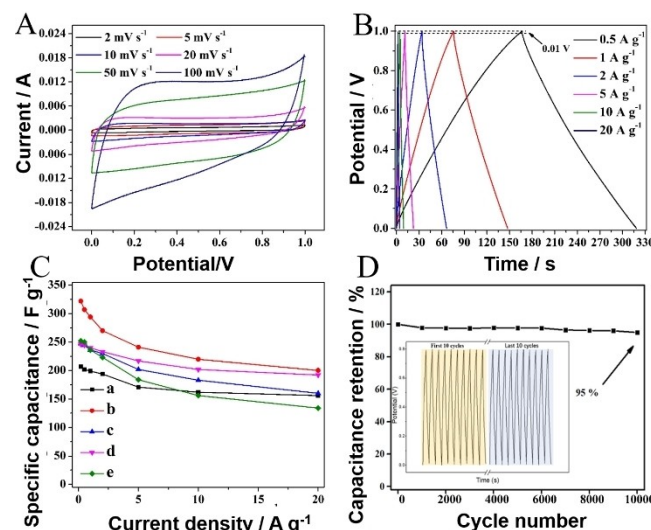


Figure 4. Two electrode system: (A) CV curves of HOMAC-3 electrode at various scan rates ranging from 2 to 100 mVs^{-1} . (B) Charge-discharge curves of the HOMAC-3 electrode at different current densities. (C) Specific capacitances of five electrodes as a function of current densities ranging from 0.2 to 20 Ag^{-1} ; (D) Cycle performance of the HOMAC-3 electrode at current density of 1 Ag^{-1} over 10000 cycles.

capacitance of 5 F g^{-1} and reduced to 2.2 F g^{-1} at 100 mVs^{-1} . This poor performance is due to undeveloped porous structure of HOMAC-0 without activation (Figure S11). Based on the above comparison, it can be confirmed that the activation of KOH plays an important role in porous carbon with excellent electrochemical performances.

In order to study the electrochemical properties of these HOMAC materials, galvanostatic charge-discharge tests in 2-electrode were performed for HOMAC electrodes at various current densities ranging from 0.5 A g^{-1} to 20 A g^{-1} as shown in Figure 4B. The detailed information for discharge profiles $5\text{--}20 \text{ A g}^{-1}$ were shown in Figure S9B. The charge-discharge curves of all the samples portrayed the quasi-isosceles triangular shape in the potential range 0 to 1 V, suggested the major contribution of double-layer capacitance.^[53,54]

Negligible IR value of 0.01 V can be obtained at 0.5 A g^{-1} due to good electrical conductivity.^[55] Figure 4C shows that the specific capacitances of five HOMAC electrodes at the current densities of 0.2 A g^{-1} are 207, 322, 247, 246 and 252 F g^{-1} , respectively. It is noticeable that the specific capacitance of HOMAC-3 electrode is the highest compared to the other electrodes. It still retains 200 F g^{-1} at high current density of 20 A g^{-1} (62% retention), confirming the rate capability of the HOMAC-3 electrode. This is because interconnected and hierarchical porous structure with thin walls not only facilitates electrolyte infiltration in HOMAC-3, but also shorten the ion migration distance, promoting the full utilization of the inner micropores.^[54,56] Figure 4D shows the cycling stability of HOMAC-3 electrode at current density of 1 A g^{-1} . It can be seen that the specific capacitance retained 95% of the initial after 10000 cycles, showing that the symmetry supercapacitor holds good cycling stability. The initial 10 cycles and final 10 cycles during 10000 continuous charge-discharge cycles are shown in the inset of Figure 4D. It can be observed that the linear symmetric triangular-shaped curves hardly changed, which reveals no distinct electrochemical change occurred during the long-term charging/discharging process.^[57]

To investigate the resistive parameters affecting the electrochemical performance of the symmetric HOMAC-3 || HOMAC-3 device, electrochemical impedance spectroscopy (EIS) tests were performed to analyse the resistance (R_e) and charge transfer resistance (R_{ct}) of the HOMAC supercapacitors. The frequency range is from 0.01 Hz to 100 kHz. The open circuit potential is 5 mV. Figure 5A shows an apparent semicircle in the high-frequency range in the EIS spectrogram of HOMAC-3 electrode over the range of 0.01 Hz to 10 kHz caused by the electric double-layer capacitance, corresponding to the charge transfer resistance (line a represents test curve and b represents the fitted curve).^[58] The R_{ct} resistance values is 0.44Ω . The low charge transfer resistance of HOMAC-3 may be attributed to the presence of a large number of ordered pores. In low frequency, the oblique line represents the ion diffusion resistance.^[59] The R_e value is 2.21Ω . The low resistances indicated the fast diffusion of electrolyte ions into the carbon porous matrix and good conductivity, which are excellent electrode materials.^[60] Figure 5B shows that the phase degree angle of HOMAC-3 electrode is about -80 degree which nears

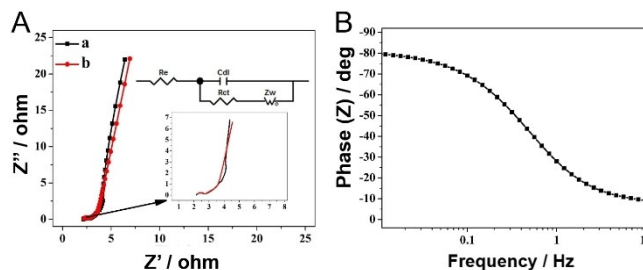


Figure 5. (A) Nyquist plots of HOMAC-3 electrode (The inset shows the magnified view of the high-frequency region and the electrical equivalent circuit used for fitting impedance spectra), the black line (a) is the real curve and the red one (b) is the fitted curve. (B) The bode phase diagrams.

to -90 degree in an ideal supercapacitor (a represents the original data, b is the fitting data), which represents the excellent electronic conductivity with an ideal capacitive behaviour, arising from the effective dispersion of electrolyte ions into the electrode materials.^[61] All these results further demonstrated the excellent electron and ion-transport behaviour of HOMAC-3 based supercapacitor. The inset displays the equivalent circuit of HOMAC-3 electrodes, where R_e , Z_{dl} , R_{ct} , and C_{dl} represent the equivalent series resistance (ESR), the Warburg resistance, the charge transfer resistance and the double layer capacitance.^[25] In summary, the optimal electrochemical performance of HOMAC-3 based symmetric supercapacitor device is primarily due to the higher specific surface area, portable porous structure and low resistance.

- (i) As a major factor deciding the storage capacity of the material, the large specific surface area could provide abundant active sites for adsorption and diffusion of charges, and consequently expanded reaction regions at interfaces, which in turn favors the formation of double layers in the carbon material.
- (ii) The high total pore volume with multifunctional interconnected porosities can sufficiently improve the usage ratio of carbon surface, thus reducing the diffusive resistance and improving rate capability performance. Wherein macropores act as ion-buffering pools, mesopores modulate the ion migration rate by providing a channel for rapid electrolyte ions transfer which effectively shortening the diffusion path, and micropores optimize the charge storage features by providing a large number of adsorption sites for electrolyte ion, leading to the highest potential for capacitance retention.
- (iii) The construction of partially graphitized structure with ordered pores strengthens the carbon network and improves the electrical conductivity of the electrode, thus having low resistance. They promote electrolyte ion diffusion and enhance cycle stability. Therefore, the electrode has good capacitive performance and charge/discharge rate.
- (iv) From the structure of biomass, long fibrous plants have branch-like structures, such as hollow tubes and vascular bundles, which have natural interconnection network in

general. The plants skeletons are stable and rich in carbon. It can subject to chemical or thermochemical treatment for the removal of its readily degradable constituents (all hemicellulose and most cellulose as well as partial lignin). The pre-carbonized biomass partly inherits the original structure, such as macropores and vascular bundle. KOH was easy to thoroughly permeated all parts of the pre-carbonization product during the impregnation process. That helped KOH activate the sample from inside to outside (especially the wall of tube and holes) rather than on the surface at high temperature. During the activation, the pre-carbonization product with primary long fiber structures generates more micropores and mesopores. Thus, most of the activated fiber walls present ordered micropores. In addition, 3D hierarchical porous carbon with large specific surface area and ordered microporous structure was obtained. This favorable multiscale interconnected pore networks containing micro/meso/micropores could provide a large inner surface for ion diffusion and adsorption and an effective path for ion and charge transfer. And the stable skeleton structure with good conductivity ensures the superior cycling stability. Accordingly, the capacity and rate performance of the electrode could be enhanced.

- (v) In addition, effective synthesis method is necessary to obtain activated carbon materials with high electrochemical performance. Without fully activation for long fibrous plants carbide, there would no high S_{BET} , V_{tot} and low resistance and no excellent electrochemical performance for supercapacitor electrode.

Besides, we proved three important factors (S_{BET} , V_{tot} and resistance) in our machine learning correct through this report. More importantly, the machine learning instructs us to choose the long fibrous plants-saussurea involucre stalk as precursor. By applying it to electrodes of supercapacitor, the long fiber plant with KOH activation is an optimal choice for electrodes of supercapacitors. Therefore, using KOH to activate long fiber plants displays many advantages, which make it appropriate to electrode with superior electrochemical properties.

It is well known that low energy density is one of main factors to hinder the commercialization of supercapacitors. To overcome this drawback, efforts are usually carried out on two directions: improve the specific capacitance and broaden its voltage window. The electrolyte has a great influence on the performance of supercapacitor, and the compatibility between electrolyte and electrode material is the decisive factor on the operating voltage of a supercapacitor. In order to further improve the energy density, symmetry supercapacitor with HOMAC-3 in 1 M Na_2SO_4 aqueous electrolyte was investigated in a symmetric two-electrode cell configuration, which possess a higher operation voltage than that in the acid or alkaline solution. Figure 6A shows the CV curves of HOMAC-3||HOMAC-3 symmetric supercapacitor at scan rate of 20 mV s^{-1} in different voltage windows. It is clear that the CV curves maintain an almost rectangular shape. There is no obvious increase of anodic current at 1.8 V. Note that even if the working potential reaches 1.8 V, the device has an ideal rate

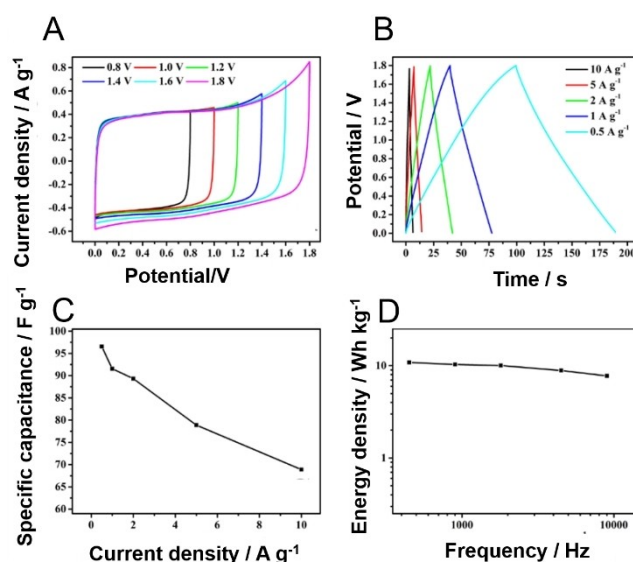


Figure 6. (A) CV curves of the symmetric supercapacitor at different voltage windows in 1 M Na_2SO_4 aqueous electrolytes at 20 mV s^{-1} . (B) GCD curves of symmetric supercapacitors at different current densities. (C) Specific capacitances of symmetric supercapacitor as a function of current densities ranging from 0.2 to 10 A g^{-1} . (D) Ragone plots of symmetric supercapacitor.

performance.^[62] The galvanostatic charge-discharge rate was tested at different current densities in Figure 6B. A slight IR drop can be observed from the approximate linear lines with symmetric triangular shapes. This indicates that the HOMAC-3||HOMAC-3 symmetric supercapacitor has low internal resistance, good rate capability and excellent electrochemical capacitance.^[63] Energy density and power density of symmetric supercapacitor are shown in the Ragone plot from Figure 6D. The specific capacitance is 96 F g^{-1} at current density of 0.5 A g^{-1} and the operating voltage is 1.8 V. The energy density of symmetry supercapacitor is 33.91 Wh kg^{-1} when the power density is 180 W kg^{-1} . When the power density is as high as 9000 W kg^{-1} , the energy density of the symmetry supercapacitor still remains 7.75 Wh kg^{-1} . These results again emphasize the optimum and usefulness of long fibrous plants activated by KOH, which exhibits a very large capacitance and high power management irrespective of the nature of the electrolyte, underscoring the possibility of future practical applications.

For better understanding, the specific capacitance of HOMAC-3 and some of those in literature reports are summarized in Table 2. Intuitively, the long fibrous plants derived carbonaceous electrodes (such as jute fiber,^[64] soybean root,^[65] Prosopis Juliflora wood waste carbon blocks,^[66] cotton cellulose,^[67] houttuynia,^[40] cotton stalk^[18] and HOMAC-3) are superior or comparable to other biomass without fibrous features, such as pine nut shells,^[68] soybean meal,^[69] potato peel,^[70] borassus flabellifer flower,^[39] alfalfa flowers,^[31] malva nut,^[42] gardenia jasminoides ellis flowers,^[71] lotus leaves,^[72] sugarcane bagasse^[73] and chitin.^[74]

Therefore, compared with others, the long fibrous plants with bigger length-diameter ratio and thinner wall are considered as promising precursors in advanced electrodes for

Table 2. Summary of electrochemical parameters of biomass derived carbon electrodes.

Biomass	S_{BET} ($\text{cm}^2 \text{g}^{-1}$)	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	R_s (Ω)	Capacitance (F g^{-1})	Current density (A g^{-1})	Electrolyte/ Electrode configuration	Ref.
Pine nut shells	1471	0.92	0.62	241	0.5	6 M KOH/3E	[68]
Soybean meal	483	0.43	0.39	360	0.2	1 M H_2SO_4 /3E	[69]
Potato peel	1911.5	1.17	2.27	128	1	1 M H_2SO_4 /2E	[70]
Borassus flabellifer flower	474.99	0.2511	/	275	1	1 M H_2SO_4 /3E	[39]
Alfalfa flowers	1590.9	1.1329	1.47	201.4	0.1	6 M KOH/2E	[31]
Malva nut	1842	0.95	0.95	279	1	6 M KOH/3E	[42]
Gardenia jasminoides Ellis flowers	1637	0.82	0.65	255	0.5	6 M KOH /3E	[71]
Lotus leaves	3601	2.44	0.78	294	1	6 M KOH/2E	[72]
Sugarcane bagasse	725	/	0.5	265	0.2	2 M KOH/3E	[73]
Chitin	1828	/	0.52	221	0.5	6 M KOH/2E	[74]
Jute fiber	1903.8	1.01	0.49	346	1	6 M KOH/3E	[64]
Soybean root	2690	1.9	0.71	328	1	6 M KOH/3E	[65]
Prosopis juliflora wood waste carbon blocks	2943.4	1.83	1.78	403.7	0.5	6 M KOH/2E	[66]
Cotton cellulose	2407	2.68	0.6	279	1	6 M KOH/2E	[67]
Houttuynia	2090	1.03	0.29	460.7	1	6 M KOH/2E	[40]
Cotton stalk	1964.46	1.03	4.72	254	0.2	1 M H_2SO_4 /2E	[18]
HOMAC	2073	0.89	2.21	320	0.2	1 M H_2SO_4 /2E	This work

supercapacitors in comparison to other ball like and sheet like biomass-based carbon electrodes. The long fibrous plants almost show proper pore structure and high specific surface area, which contributing to high capacitive performance. This indicates that activated carbon derived from long fibrous plants always have large specific surface area, low resistance and large pore volume. Precursor materials with long fibrous could have excellent electrochemical performance.

In order to explore the relationship between activated carbon materials and ion transmission rate, H^+ transfer rate of HOMAC-3 and cotton stalk carbon are compared.^[18] The relationship can be expected since hydraulic conductivity mainly depends on the pore sizes, whereas diffusion depends on the porosity of the activated materials. It is reflected by the pH value, the rate of H^+ through materials. Figure 7 shows that pH value of the electrodes made by activated carbon from saussurea involucrata fell down faster than the activated carbon electrodes made by cotton stalk. It is indicated that HOMAC-3 has faster ion transmission speed and more suitable pore structure of H^+ transmitting than activated carbon obtained from cotton stalks. This is why HOMAC-3 has better electrical performance than that of cotton stalk. In order to show the rate of H^+ in two materials more directly, we use Fick's second law of diffusion:

$$c = \frac{c_2}{2} \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (4)$$

The c_2 expresses the H^+ concentration equipped with sulfuric acid, x expresses the thickness of the electrode material, t is the diffusion time, and D expresses the diffusion coefficient

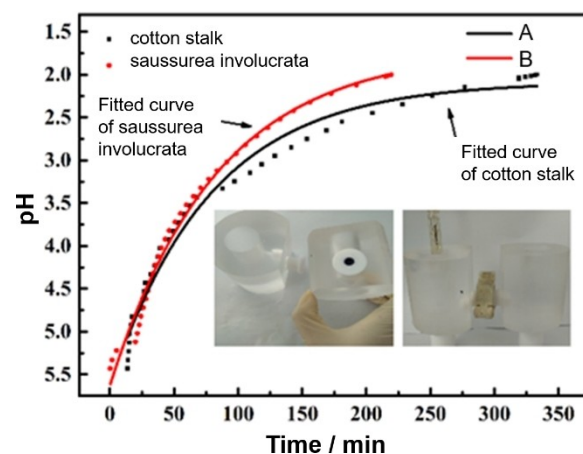


Figure 7. The change curve of pH rate with cotton stalk and saussurea involucrata. The pH curve of (A) cotton stalk; (B) saussurea involucrata. The two small figures (insert) in the bottom are the experimental devices.

of ions on the material. After calculation, we found that the diffusion coefficient of ions on HOMAC-3 is $5.074 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ ($x = 0.097 \text{ mm}$). It is 2.5 times of cotton stalk $1.547 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ ($x = 0.066 \text{ mm}$). This indicates quicker transmitting of H^+ in HOMAC-3. In order to prove the difference between the two samples in detail, we define the term k which is inversely proportional to H^+ transfer rate of the solution:

$$k = \frac{\varphi \cdot \delta}{I_e} = \frac{1}{\int_5^2 (10^{-\text{pH}2} - 10^{-\text{pH}1}) dt} \quad (5)$$

The t is time of ion diffusion, ϕ is porosity of material. l_e is actual distance of material, δ is permeability of the medium. Obviously, k is proportional to ϕ and the permeability of the medium δ , and inversely proportional to l_e . The δ/l_e could indicate the degree of difficulty of the medium passing through the material. We define δ/l_e of HOMAC-3 as b . We found that δ/l_e of cotton stalk is 0.57 b . According to that data, although the porosity of cotton stalk is higher than that of HOMAC-3, H^+ can pass through HOMAC-3 more easily.

According to the evolution formula of the Fick's first law we also know that:

$$D = D_{aq}\phi^m \quad (6)$$

The D_{aq} expresses 1 M diffusion coefficient of sulfuric acid in water while ϕ expresses porosity. We calculated that the m of cotton stalk (m_c) which is equal to $0.235 + 1.11m_s$ (m_s of HOMAC-3). So the count of hole which ions can pass in HOMAC-3 is more than cotton stalk's.^[75] The HOMAC has better ion permeability, leading ions through HOMAC faster during the rapid charge and discharge process, thus getting better specific capacitance.

By combining the imaginary (C'') plots of the HOMAC-3-based and cotton stalk-based capacitors (Figure S12), we can further prove that the structure of the carbon made by *saussurea involucrata* is more conducive to the transport of ions. The imaginary part of capacitance goes through a maximum at frequency f which defines the relaxation time constant t ($= 1/f$) and marks the point where the resistive and capacitive impedance are equal.^[56] The $t=2.6$ s for HOMAC-3 electrode is smaller than that of cotton stalk carbon electrode (31 s). Both HOMAC-3 based electrode and cotton stalk based electrode have a large specific surface area ($2073.36 \text{ m}^2 \text{ g}^{-1}$ and $1964.46 \text{ m}^2 \text{ g}^{-1}$), but the HOMAC-3 is characterized with better rate performance due to fast ion kinetics within short channels.^[65,76] The rapid frequency response of HOMAC-3 capacitor clearly indicates that the carbon structure of HOMAC-3 electrode with plenty of nanopores on the surface can potentially shorten the diffusion lengths, promote the electron migration, thus enabling fast ion and electron transport within the interior of electrode. This is consistent with the results shown in Figure 7.

Combined with our previous work (Table S2), both long fibrous plants-based porous carbon materials have large specific surface area (larger than $1900 \text{ m}^2 \text{ g}^{-1}$), high pore volume (higher than $0.89 \text{ cm}^3 \text{ g}^{-1}$) and low resistance (4.72Ω and 2.21Ω), showing characteristic of electrical double layer capacitance, and the *saussurea involucrata* stalk-based porous carbon obtain highest specific capacitance of 320 F g^{-1} , which fits well with our prediction of machine learning. From these results, we can conclude that long fiber plants are promising biomass precursor of electrodes for high performance supercapacitors.

3. Conclusion

The activated carbon materials obtained from long fibrous plants have a very high charge storage capability with high specific capacitance of 320 F g^{-1} and energy density of 33.91 Wh kg^{-1} . This high capacitance can be attributed to the high specific surface area ($2073.36 \text{ m}^2 \text{ g}^{-1}$), large pore volume ($0.89 \text{ cm}^3 \text{ g}^{-1}$) and small resistance (2.21Ω). This work corresponds to our prediction by machine learning, which the three most critical factors in making high performance supercapacitors include specific surface area (S_{BET}), pore volume (V_{tot}), internal resistance (R_s). By discussing the effect of fibrous plants as precursor on the physicochemical properties and electrochemical performances of the final activated carbon samples, we also demonstrate that long fibrous plants as precursors have obvious advantages in preparing activated carbon with high specific surface area and high degree of graphitization. The plants with long fibrous features could be used as a potential biomass carbon sources for the preparation of electrode materials with high-performance supercapacitors. This result can improve the selection efficiency from thousands of biomass precursors and supply a reference in preparation of biomass carbon material.

Supporting Information Summary

Detail information of experimental section, electrochemical performances in electrolyte can be found in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: long fiber plants • micropores • *saussurea involucrata* stalk • carbon • supercapacitors

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