Microbial Porous Carbon by Low-Alkali Activation for Flexible Supercapacitors

Diwen Zhu¹ · Junwen Hou¹ · Lijin Zhang¹ · Yanfeng Gao¹ · Bingru Dai¹ · Yue Lian² · Haishui Yan¹ · Huaihao Zhang²

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Abstract

Chlorella is a genus of algae widely distributed in fresh water, with high yield and low cost. In this work, using a green and low-alkali approach, high-economic-value porous carbon is transformed from *Chlorella* precursor, revealing superior electrochemical performance. More precisely, *Chlorella*, with an intrinsic micron-scale structure, provides a good basis for the preparation of carbon materials with high specific surface area. Then, various components (proteins, fats, vitamins and others) of algae provide a large number of heteroatomic defects and surface functional groups after carbonization, thus offering additional pseudocapacitance of porous carbon. Finally, low-alkali activation reduces the corrosive damage to equipment, confirming the environmental protection trend.

Graphic Abstract

Keywords Algae · green activation · porous structure · flexible supercapacitors

✉ Huaihao Zhang
huaihaozhang@163.com

Extended author information available on the last page of the article

Introduction

The depletion of fossil fuel reserves has accelerated the research and development of renewable energy conversion and storage equipment to meet the urgent energy needs.^{1,2} Due to the demand for rapid energy storage and long cycle life, supercapacitors (SC) are an increasing focus of research.^{3,4} Generally, SCs depend greatly on the characteristics of the electrode materials.⁵ A well-designed structure with suitable aperture distribution for electrode materials is very important for high-performance supercapacitors.⁶ Based on economic and sustainable development goals, activated carbon (AC) derived from biomass has been identified as a promising commercial SC electrode material.^{7–9} Therefore, an abundant and cheap biomass source is important for the stable preparation and application of activated carbon.^{10,11} However, traditional biomass carbon preparation methods are not suitable for large-scale and green applications, due to their complex manufacturing processes, the use of highly corrosive chemical reagents, and the special equipment required.^{12,13}

In general, compared with previous carbon materials derived from conventional fossil by-products (such as coal, petroleum coke and asphalt), the cost of biomass carbon materials precursors is usually lower.^{14,15} At present, direct carbonation-activation is a very common way to synthesize porous carbon from biomass.^{16,17} Specifically, the precursors are firstly carbonized in an atmosphere of flowing inert gas, and are then activated either physically (such as CO₂ or vapor) or chemically (such as KOH, ZnCl₂ or H₃PO₄) at relatively high temperatures.^{13,18,19} As a result, the obtained carbon materials exhibit highly interconnected porous structures and large specific surface areas.²⁰ However, these methods often involve high energy consumption, extensive corrosion and excessive activator usage, leading to high costs, serious pollution and other problems.²¹ Therefore, the green activation method has attracted wide interest in the practical application of biomass carbon.

In this work, *Chlorella* was employed as precursor to prepare active porous carbon (PC) by low-alkali hydrothermal carbonization. *Chlorella* is a genus of algae widely distributed in fresh water, even leading to ecological damage by its overgrowth in some areas. As a microbe, its micron size and abundant ion transport channels on the surface allow alkali to enter its bulk phase deeply during the hydrothermal process, ensuring effective activation to develop a porous structure. *Chlorella*-based PC has some advantages over activated carbon produced by

conventional methods: (1) The varied composition of *Chlorella* (protein, fat, vitamin and others) can produce a large number of heteroatom defects and oxygen-rich functional groups by a low-alkali method, offering additional pseudocapacitance.²² (2) The activation approach using low temperature and less alkali is better able to satisfy green and environmental protection requirements, and also reduces costs and improves safety. The PC obtained in this work has excellent electrochemical activity, showing high capacity and energy density.

Experimental

First, impurities were removed by deionized (DI) water, followed by drying at 60°C for 12 h. The solution with *Chlorella* (1 g) and KOH was transferred into an autoclave (100 mL) and heated in an oven at 120°C for 6 h. After cooling to room temperature, the solid filtration was collected and freeze-dried for 1 day. The obtained products were annealed at 650°C for 2 h (heating rate of 2°C min⁻¹) under N₂ atmosphere. Finally, the aterrimus materials were thoroughly washed with 10% HCl solution until slightly acidic, and then dried at 60°C. The as-prepared samples were denoted as PC.

Physical characterization and electrochemical test details are presented in the supporting information.

Results and Discussion

Chlorella carbon was etched into a porous structure by KOH (Fig. 1). After this step, the porosity of the carbon is further improved during the subsequent gasification process. Moreover, some potassium ions are able to enter the carbon lattice and form intercalated potassium or other potassium compounds, which generate amorphous porous structures after washing. In this work, the intrinsic ion exchange channels on the surface of algae absorb KOH solution into the body phase. The suitable hydrothermal surroundings promote the entry of potassium ions into the carbon lattice to achieve adequate activation, thus forming amorphous porous structures. Accordingly, compared with conventional chemical activation mode, the hydrothermal process can enable greener activator usage. Therefore, its activation and carbonization remain highly efficient at relatively low temperatures.

As clearly observed and analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 2), PC with a combination of a large gully and small pore channels exposed more electrochemically active

Fig. 1 Schematic diagram of PC prepared by hydrothermal synthesis with less alkali.

sites (Fig. 2a and b). Benefitting from the surficial functional groups, the infiltration of electrolyte and the adsorption and transmission of charged particles were greatly improved. Secondly, the hole on the PC surface extended deep into the carbon interior to form an electrolyte infiltration channel, effectively activating the internal space and improving the spatial utilization of PC (Fig. 2e and f). In terms of its morphology and structure, PC prepared at low temperature and with less alkali has highly developed pores and a rough surface, both of which facilitate the electrolyte infiltration and ion adsorption inside the material.²³ In addition, the *Chlorella* carbon (see supplementary Figure S6) was prepared by the same procedure without alkali. Without the participation of KOH, there was no obvious pore structure in the prepared carbon material (CM). Based on SEM, the structure of CM is relatively compact and presents as a nonporous massive structure. It is not conducive to the accumulation of double-layer capacitance.

The x-ray diffraction (XRD) patterns (Fig. 3a) of PC show a broad peak centered at 23° that can be assigned to the graphite plane (002), and the peak at 43° is attributed to a weak disordered plane (100), suggesting its amorphous or disordered structures.²⁴ Raman spectra (Fig. 3b) further verified this conclusion. The two distinct peaks at $\sim 1350\text{ cm}^{-1}$ (D band) and $\sim 1590\text{ cm}^{-1}$ (G band) represent the disordered and graphitic texture, respectively. Simultaneously, the intensity ratio of the D-band and G-band (I_D/I_G) of PC is ascribed to potassium intercalation and the introduction of numerous nanopores from the activation process.^{16,25} The value of I_D/I_G is 0.92, demonstrating a high defect degree. Clearly, the formation of disordered structures during the

activation process enhances the active site exposure and ion diffusion.

Again, x-ray photoelectron spectroscopy (XPS) was further employed to prove the element composition and valence bond relationship. The broad spectrum in Fig. 4a reveals the existence of C, O, N and P. In C 1s spectra (Fig. 4b), the valence bond relationships of C, N and O, including C–C (284.4 eV, $\sim 71.43\text{ at.}\%$), C–N (285.1 eV, $\sim 6.35\text{ at.}\%$), C–O (286.1 eV, $\sim 15.13\text{ at.}\%$) and C=O (288.6 eV, $\sim 7.08\text{ at.}\%$), suggest the strong association between heteroatoms (N and O) and C. As is well known, heteroatoms make the carbon rich in defects, which is helpful in improving the pseudocapacitance.^{26,27} Similarly, the peak positions (Fig. 4c) at 532.4 eV (C–O), 531.0 eV (C=O) and 535.4 eV (O–C=O) also confirm the abundance of O-containing functional groups on the carbon surface.²⁸ The high-resolution N 1s spectrum (Fig. 4d) can be deconvoluted into four sub-peaks. The main peak at 399.5 eV is attributed to pyrrolic N, and the peaks centered at 397.8 eV, 400.6 eV and 402.7 eV can be ascribed to surface oxygen and nitrogen groups (designated as pyridinic N, N–Q and N–X, respectively).¹⁶ The N-heteroatom defect constructed in the carbon lattice activates a variety of electroactive sites and enhances the conductivity by unpaired electrons. In summary, PC prepared using *Chlorella* with abundant heteroatom defects and functional groups enhances the hydrophilic and pseudocapacitance properties.

The Fourier transform infrared (FTIR) spectrum (see supplementary Figure S3) also gives various functional group responses consistent with the XPS results. The characteristic peaks at 1089 cm^{-1} and 1830 cm^{-1} correspond to the

Fig. 2 SEM images (a–d) and TEM micrographs (e–f) of PC after activation.

Fig. 3 (a) XRD pattern and (b) Raman pattern of PC.

Fig. 4 XPS spectra of PC: (a) C 1s; (b) N 1s; (c) O 1s and (d) P 2p

stretching vibrations of C–O and C=O, again confirming the existence of O-containing functional groups. The bending vibration in the N–H surface at 1560 cm^{-1} and the hydrogen bond association between $3300\text{ cm}^{-1} \sim 3000\text{ cm}^{-1}$ form the strong binding force between the carboxylic acid hydroxyl group and hydrogen, thus enhancing the affinity between carbon material and electrolyte and facilitating electrolyte ion transmission and adsorption.²⁹

A three-electrode system is used to test the electrochemical properties of polycarbonate in 6 M KOH solution. The cyclic voltammetry (CV) curves (Fig. 5a) display nonstandard rectangular-like shapes, which are the representative characteristics of pseudocapacitance behavior induced by surface nitrogen and oxygen functional groups. Specifically, the CV curves of PC from 5 s^{-1} to 100 mV s^{-1} do not show apparent distortion, suggesting its excellent rate capability. Figure 5b depicts the imperfect isosceles triangular galvanostatic charge–discharge (GCD) curves of PC, implying the characteristic of Faradaic pseudocapacitance

as well, consistent with CV curves. The specific capacitances at scan rates of 5 mV s^{-1} , 10 mV s^{-1} , 20 mV s^{-1} , 50 mV s^{-1} and 100 mV s^{-1} are calculated to be 316.9 F g^{-1} , 306.5 F g^{-1} , 293.9 F g^{-1} , 275.5 F g^{-1} and 250.8 F g^{-1} , respectively. Furthermore, the specific capacitance of PC, higher than that of some carbon-based electrodes (see supplementary Table S1), might ascribe to the synergistic effect between three-dimensional (3D) interlinked porous, surface beneficial functional groups and defect structures. Simultaneously, abundant defects introduced by nitrogen and oxygen functional groups enhance the surface wettability and provide more active sites of the carbon layer during the charge–discharge process. The Nyquist plot of PC is displayed in Fig. 5c to further investigate the conductivity of 3D interlinked PC. Herein, nearly vertical lines of PC at low frequency represent the dominance of electrical double-layer charge storage. PC has a small semicircle at high frequency, implying its outstanding electrical conductivity with low ion diffusion resistance and charge transfer resistance.

Fig. 5 Electrochemical properties of PC: (a) CV curves and (b) GCD curves; (c) Nyquist plot (partial magnified Nyquist plots); (d) The first 12 GCD cycles at 2 A g^{-1} .

Notably, this result can be attributed to the abundant interconnected pores for ion transport, which are conducive to charge transfer and ion diffusion on the electrode surface. As described in Fig. 5d, the coulombic efficiency of PC is close to 100%. During the initial 12 cycles, the GCD of PC is highly symmetrical and repeatable, demonstrating its good electrochemical reversibility.

The electrochemical performance of the symmetric solid-state supercapacitors (PC//PC) was tested (see supplementary Figure S5). The CV curve of PC//PC (Fig. 6a) displays a rectangle-like curve without obvious polarization under different potential windows, showing its good rate performance. The CV curves (Fig. 6b) displayed similar shapes at different scan rates, implying the stability and dynamics of ion transport. Compared with that in the three-electrode system, the certain deviation (Fig. 6c) in the linearity of the GCD curves proves the increased charge transfer resistance between the PC electrode and the gel electrolyte. PC//PC capacitors obtain high capacitance (39.6 F g^{-1} at 0.3 A g^{-1}), maintaining 73.8% (26.6 F g^{-1} at 5 A g^{-1}) even at high

current densities. Its Ragone plots delivered high energy density and power density of 13.54 Wh kg^{-1} and 10.01 W kg^{-1} , respectively, as shown in Fig. 6d. The overall results proved PC//PC a prominent electrode material for electrochemical capacitors.

Conclusions

In summary, a porous active carbon with a 3D structure has been successfully synthesized from *Chlorella* precursor through hydrothermal and low-alkali activation methods. In the hydrothermal treatment process, KOH diffused into the *Chlorella* body phase as an activator, reduced the stack and agglomeration, and generated a porous network structure through green activation. The 3D porous structure of as-obtained PC can offer abundant active sites and open diffusion channels, accelerate the charge accumulation rate, and relieve the electrode volumetric effect. In short, PC has splendid electrochemical performance, including remarkable

Fig. 6 Capacitive performances of PC//PC flexible supercapacitor: (a) CV curves in varied opening voltages at 50 mV s^{-1} ; (b) CV curves at various scan rates; (c) GCD curves at different opening voltages at 0.3 A g^{-1} ; (d) GCD curves at different current densities.

cycle stability, ideal charge storage capacity, and good rate performance. Hence, this convenient activation method is conducive to the efficient production of materials derived from biomass carbon precursors for supercapacitors.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11664-021-09213-y>.

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Conflict of interest All the authors are students of Guangling College and Yangzhou University (except for the corresponding author). The authors declare that they have no conflict of interest.

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Authors and Affiliations

Diwen Zhu¹ · Junwen Hou¹ · Lijin Zhang¹ · Yanfeng Gao¹ · Bingru Dai¹ · Yue Lian² · Haishui Yan¹ · Huaihao Zhang²

¹ Chemical and Medicine Department, Guangling College, Yangzhou University, Yangzhou 225009, People's Republic of China

² School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, People's Republic of China