Yeast-Based Porous Carbon with Superior Electrochemical Properties

Yuhong Tian,* Qiaoxia Ren, Xiaoyu Chen, Linbo Li, and Xinzhe Lan

ABSTRACT: Biomass is a promising carbon source for supercapacitor electrode materials due to its abundant source, diversity, and low-cost. Yeast is an elliptic unicellular fungal organism that is widespread in nature. In this work, we used yeast as the carbon source and Na$_2$SiO$_3$ as the activator to prepare a honeycomb porous carbon with higher surface area. The yeast and Na$_2$SiO$_3$ were directly mixed and ground without any solvent, which is simple and characterized by large-scale application. The prepared porous carbon shows a good specific capacity of 313 F/g in 6 M KOH at a density of 0.5 A/g and an excellent rate capability of 85.9% from 0.5 to 10 A/g. The results suggest that the yeast-derived porous carbon may be a promising sustainable bio-material for the preparation of supercapacitor carbon electrode materials. This study provides an economical and practical avenue for yeast resource utilization and develops a simple approach to prepare porous carbon materials.

1. INTRODUCTION

Currently, the use of clean and renewable energy has aroused widespread attention with the increasing problems of energy consumption. As an electrochemical energy storage device, supercapacitors have developed rapidly.1−3 For the typical supercapacitor, an electrode material is one of the important parts, which is a research point for the majority of researchers in the field of supercapacitors. Generally, carbon materials are the most commonly used electrode materials in supercapacitors because of their diverse shapes, controllable, non-toxic, and high electrical conductivity.4−8 Biomass, a renewable clean carbon source, has been shown to be used to prepare high-performance electrode materials for energy storage systems.9 In the past few years, many outstanding work on the preparation of biomass-based carbon electrodes has received much attention. Examples such as tofu,10 cotton,11 flour,12 onions,13 elm flower,14 cornstalk,15 coconut shell,16 and synthetic carbon materials are assembled into supercapacitor electrodes for potential energy storage applications.9 In the past few years, many outstanding work on the preparation of biomass-based carbon electrodes has received much attention. Examples such as tofu,10 cotton,11 flour,12 onions,13 elm flower,14 cornstalk,15 coconut shell,16 and synthetic carbon materials are assembled into supercapacitor electrodes for potential energy storage applications.

For the preparation of biomass porous carbon, direct pyrolysis and activation methods are generally available. However, direct pyrolysis has many inevitable problems such as severe shrinkage of biomass precursors, resulting in pore collapse, morphological fragmentation, and low surface area, lack of active sites, and so on. To improve the surface area and richness of pore structure of biomass-derived carbon materials, there are currently two methods of chemical activation or physical activation. Generally, the former is a common and effective pathway. Chemical activators such as NaOH, KOH, Na$_2$CO$_3$ and K$_2$CO$_3$ are the most commonly used for the preparation of target materials.17−19 However, traditional activators are mostly toxic and corrosive, and it is often etched quantity of the carbon substrate and mass production during activation, which will undoubtedly lead to the collapse of the pore structure, low yield, and broken morphology.20−22 Therefore, one of the promising but challenging research directions is to maintain a large surface area without sacrificing the natural structure of biomass-based carbon during the preparation of porous carbon. New strategies that prepare biomass-derived carbon materials with a good pore structure and high surface area should be continued to be developed.

Yeast is a kind of single-celled spherical fungal organism, which is widely used in wine, food, medicine, cosmetics, and other fields. In recent years, as the rising yeast industry is linked to human life, it is excessively produced (over 3 million tons), leading to large amounts of yeast that are either wasted or used as animal feed.18−20 Considering that yeast has a similar subcellular structure to higher animal and plant cells, it can be directly converted into carbon materials by pyrolysis. Furthermore, it is easy to culture, green, and has a fairly uniform morphology, which can be used as a sustainable biomass material to prepare carbon electrode materials for supercapacitors.

Received: September 23, 2021
Accepted: December 14, 2021
Published: December 27, 2021
Herein, an approach for large-scale synthesis with a low-cost sodium silicate (Na$_2$SiO$_3$) activator was used to prepare a honeycomb porous carbon derived from yeast. The Na$_2$SiO$_3$ played important roles as an activation agent and porogen to create a rich porous structure. The mixing of sodium silicate with yeast only involves consolidation, pyrolysis, and washing treatment, and as a solvent-free process, it facilitates mass-scale production.

2. RESULTS AND DISCUSSION

2.1. Morphology and Structure Characterization. The mixing of Na$_2$SiO$_3$ and yeast is carbonized at a high temperature; Na$_2$SiO$_3$ particles act as pore creators during the following activation process. Figure 1a–c shows the SEM images of PC-0.3-800 at different magnification indices. PC-0.3-800 shows a honeycomb structure, which is connected by holes with different pore sizes, and the structure is relatively fluffy. Porous carbon with distinct pore size of the honeycomb structure is more conducive to electrolyte exchange.\textsuperscript{26,27} Additionally, the direct exposure of honeycomb porous carbon to the electrolyte may efficiently shorten the ion diffusion pathway and lower its resistance. XRD is applied to investigate the crystal structure of the obtained carbon materials. Figure 1d demonstrates the XRD pattern of PC-0.3-800, showing that the two broad peaks are located at approximately $2\theta = 23.8$.
and 43.7°, pointing to the (002) and (101) reflections, respectively. Figure 2b,c is the EDX mapping of PC-0.3-800, which shows that the C and O elements are evenly distributed on the surface of the carbon material. Figure 2d is the EDX element composition of PC-0.3-800, which further shows that the sample mainly composed of C and O elements. A small amount of Si and Na elements were present because the washing was not thorough enough to cause complete removal of Na2SiO3.

Figure 3a is the FTIR spectrum of samples prepared at different activated temperatures. There are three obvious absorption peaks. The band observed at 1730−1640 cm\(^{-1}\) is assigned as the carbonyl functional group (aldehydes, esters, ketones, and carboxylic acids compounds) in carbon materials. The band at 1425 cm\(^{-1}\) is ascribed to the stretching vibrations of C=\(\equiv\)C or the aromatic ring, which indicates the presence of carbonyl-containing groups and the aromatization of the precursor. The absorption peak located at 1064 cm\(^{-1}\) is the C−O stretching vibration. This band is clearly observed only at PC-0.3-700, indicating that ether, esters, alcohols, and phenol would break down and that the C−O band would disappear at high temperatures.

The degrees of graphitization of the PC-0.3-800 is demonstrated by Raman spectroscopy (Figure 3b). Two characteristic peaks belonging to the D and G bands of carbon can be observed. The D-band (1360 cm\(^{-1}\)) is related to a disordered or defective graphite structure, while the G-band (1597 cm\(^{-1}\)) belongs to ordered sp\(^2\)-bonded carbon atoms. Generally, the intensity ratio between the two bands (marked as \(I_D/I_G\)) represents the graphitization degree of carbon materials. For PC-0.3-800, the highest \(I_D/I_G\) value (1.21) indicates a supreme graphitization degree, and the relatively high graphitization degree could endow PC-0.3-800 with enhanced conductivity.

The nitrogen isothermal adsorption/desorption test is applied to investigate the porous structure of PC-0.3-800. The adsorption−desorption isotherms of PC-0.3-800 are presented in Figure 4a; the isotherms of PC-0.3-800 exhibit combined feature of type I and type IV sorption isotherms. At \(P/P_0 < 0.1\), a sharp increase in the amount of absorbed nitrogen indicates that there are a large number of micropores in the porous carbon. Moreover, the H4-type hysteresis loop at \(P/P_0 \sim 0.42−0.95\) suggests the existence of a certain number of mesopores. Figure 4b shows the pore size distribution of the PC-0.3-800 by Barrett−Joyner−Halenda (BJH) analysis, which further reveals the presence of mesopores.

2.2. Electrochemical Performance. The electrochemical tests are applied to verify the effect of the Na2SiO3 dosage and activated temperature in activated processes on electrochemical performance. As shown in Figure 5a,b, the CV curves of all obtained materials were almost rectangular shape at the same scan rate, showing superior EDLC (electrochemical double layer capacitors) behavior.

Significantly, the discharge time of PC-0.3-800 is the longest, reflecting the highest adsorption/desorption capacity of electrolyte ions during electrolysis, which is consistent with the CV results. Moreover, the corresponding specific
capacitances calculated by discharge branches are summarized in Figure 5e,f. Obviously, PC-0.3-800 possesses excellent energy storage performance (313 F/g) and outstanding rate capability of 85.9% from 0.5 to 10 A/g, which is better than other carbon-based materials (Table S1). In addition, the lowest capacitance of PC indicates the important role of Na₂SiO₃ as the activator.

Further, EIS (electrical impedance spectroscopy) measurements were employed to explore the conductivity in the open circuit voltage, which is shown in Figure 5g,h. The profile is composed of two parts: one is a linear part in the low frequency region, which is related to the diffusion resistance of the electrolyte ions, the other is the half circle of the high frequency region, which is associated to charge transfer.

Figure 5. Electrochemical evaluation of the materials: (a,b) CV curves at the same scan rate; (c,d) GCD curves at same current density; (e,f) specific capacitances at different GCD current densities; (g,h) Nyquist plots.
resistance.\textsuperscript{41,42} Obviously, the almost-vertical line of PC-0.3-800 at the low frequency range reflects ideal capacitive behavior, and PC-0.3-800 shows a low charge transfer resistance (about 0.68 \( \Omega \)) at high frequency range. The cycle life diagram of PC-0.3-800 is shown in Figure S2, and after 5000 GCD cycles, the specific capacitance can still be maintained at around 91.8%.

3. CONCLUSIONS

In summary, an approach for large-scale synthesis with low-cost sodium silicate (\( \text{Na}_2\text{SiO}_3 \)) activator was used to prepare a honeycomb porous carbon derived from yeast. As an effective activator, \( \text{Na}_2\text{SiO}_3 \) plays an important role in preparing porous carbon materials with a rich pore structure. The effects of mass ratio and pyrolysis temperature of different \( \text{Na}_2\text{SiO}_3 \) to yeast on the electrochemical properties of yeast-based porous carbon are investigated. PC-0.3-800 shows high performance (313 F/g) generated by the carbon-based electrodes and an outstanding rate capability of 85.9\% from 0.5 to 10 A/g. Moreover, the specific capacitance can still be maintained at about 91.8\% after 5000 GCD cycles. This study provides an economical and practical avenue for yeast resource utilization and develops a simple approach to prepare porous carbon materials.

4. EXPERIMENTAL SECTION

4.1. Materials. Yeast (\textit{cerevisiae} cells) was purchased from Angel Yeast Co., Ltd; \( \text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} \) (AR) and HCl were purchased from Fuchen Chemical Reagent Co., Ltd, Tianjin.

4.2. Preparation of Porous Carbon. Usually, yeast was first washed several times with deionized water and absolute ethanol and then dried at 60 °C. The yeast was mixed with \( \text{Na}_2\text{SiO}_3 \) in a mass ratio of 1:0.3 via grinding for 30 min in an agate mortar. The mixture was put into a tubular furnace and heated in \( \text{N}_2 \) atmosphere at 800 °C for 2 h at a heating rate of 5 °C/min. After completion, the samples were repeatedly washed with concentrated HCl (1 M) solution and deionized water to pH 7.0, dried in an oven at 60 °C for 12 h, and then collected.

The comparative samples after the same activation process were recorded as PC-\( X-Y \) (\( X \): the mass ratio of \( \text{Na}_2\text{SiO}_3 \) to yeast, \( Y \): the activation temperature). In order to study the effect of activation temperature, we obtained the samples of PC-0.3-\( t \), where \( t \) represents the activation temperature (700 and 900 °C). In addition, for the sake of comparison, the pure biochar without \( \text{Na}_2\text{SiO}_3 \) directly carbonized at 800 °C was named as PC. A schematic diagram of the sample preparation is shown in Scheme 1.

4.3. Electrochemical Tests. This paper used a three-electrode system (counter electrode: platinum plate, reference electrode: saturated calomel electrode) on the electrochemical workstation to conduct electrochemical experiments in the electrochemical workstation. The electrolyte was 6 M KOH aqueous solution. The preparation method of the working electrode was as follows: the obtained material (80 wt \%), polytetrafluoroethylene (10 wt \%) and acetylene black (10 wt \%) were mixed, and a certain amount of ethanol was added to the mixture to form a paste to prepare the working electrode. Then, the slurry is coated on foam nickel (1 cm × 1 cm) and dried in vacuum at 60 °C for 24 h.\textsuperscript{43} The electrochemical performance was characterized by CV (cyclic voltammetry), GCD (galvanostatic charge discharge), EIS (electrochemical impedance spectroscopy), and cyclic stability test.\textsuperscript{44} The total specific capacitance (\( C, \text{F/g} \)) of the electrode was calculated from the GCD curves by eq 1

\[
C = \frac{1}{m\Delta V} \frac{\Delta t}{\Delta V}
\]

where \( I \) (A) is the discharge current, \( \Delta t \) (s) is the discharge time, \( \Delta V \) (V) is the potential range, \( m \) (g) is the mass of active material on a single electrode.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05278.

Material characterization and supplement of more electrochemical data about PC-0.3-800 and its comparison of specific capacitance of the PC-0.3-800 electrode with other carbon-based electrodes (PDF)

AUTHOR INFORMATION

Corresponding Author
Yuhong Tian — School of Chemistry and Chemical Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China; orcid.org/0000-0002-2647-2466; Email: tiantianyuhong@163.com

Authors
Qiaoxia Ren — School of Chemistry and Chemical Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China
Xiaoyu Chen — School of Chemistry and Chemical Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China
Linbo Li — School of Metallurgical Engineering, Xi’an University of Architecture and Technology, Xi’an 710055, China
Xinzhe Lan — Research Centre on Metallurgical Engineering and Technology of Shaanxi Province, Xi’an 710055, China

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c05278
supercapacitors. Porous Carbon for High-Performance Supercapacitors.

This work was supported in part by the Shaanxi Provincial International Science and Technology Cooperation Project of China (grant no. 2019KW-049) and the joint Fund Project of Shaanxi Natural Science Basic Research Program and Shaanxi Coal and Chemical Industry Group Co., Ltd. (grant no. 2019JLM-42) and Xi’an Science and technology planning project (grant no. 21XJZZ0036).

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