Sustainable Lignin-Derived Hierarchical Porous Carbon for Supercapacitors: A Novel Approach for Holding Electrochemical Attraction Natural Texture Property of Precursor

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ABSTRACT: Finding low-cost and environmentally friendly precursors that can maintain their electrochemical attraction natural texture properties while obtaining hierarchical porous carbons with high electrochemical performance is desirable for offering a leap forward in industrial applications. However, phenomena associated with the high microporosity of porous carbon remain. Herein, the protective effect of hydrothermal methods and the micropore-forming ability of KOH were used. The as-synthesized porous carbon (PC-1) holds the natural texture property (the retention of texture property with apertures higher than 2 nm was up to 80%) and achieves three-dimensional (3D) architecture with hierarchical structures accompanied by an ultrahigh specific surface area (3559.45 m²/g). Benefiting from its texture properties, PC-1 possesses a high specific capacitance of 288.75 F/g at 0.5 A/g, excellent rate capability as high as 223.72 F/g at 10 A/g, and remarkable conductivity in a three-electrode system with a 6 M KOH electrolyte. In view of its environment friendliness, low cost, and excellent specific capacitance, PC-1 has promising applications in high-performance supercapacitors.

1. INTRODUCTION

Supercapacitors are a new type of energy storage devices whose performance is between traditional capacitors and batteries.1 They possess the advantages of conventional capacitors and batteries, exhibiting high power density, high energy density, and excellent cycle stability.2−5 Other attractive properties of supercapacitors are their cleanliness, high efficiency, and environment friendliness, which are unmatched by traditional energy storage devices.6,7 Carbonaceous materials (e.g., porous carbon, graphene, and carbon nanotube) have presented great potential for supercapacitor applications ascribing their high specific capacitance, long service life, and excellent chemical stability.8,9 Compared with carbon nanotube and graphene, porous carbon has highly competitive advantages owing to its high specific surface area, tunable pore structure, good electrical conductivity, and low synthesis cost.10,11

Renewable porous carbon precursors have received relatively more attention, especially as a low-cost feedstock with electrochemically attractive structures, such as wood with natural multichannel and leaves with crumpled surfaces.12,13 To enhance their specific surface area, chemical or gaseous activation is usually utilized for creating micropores.14,15 Deng et al.16 synthesized phenolic resin-derived porous carbons for capacitors using KOH as an activator, and their microporosity is in the range of 71.97−86.52%. Luo et al.17 prepared chitin-derived porous carbon for supercapacitors employing CuCl₂ as an activator, and its microporosity is as high as 96.80%. Rashidi et al.18 used CO₂ to assist the synthesis of palm kernel shell-derived porous carbon, and the results indicate that the microporosity of palm kernel shell-derived porous carbon is ~70%. The mentioned works have made significant progress in the synthesis of porous carbon with abundant micropores. As is known, micropores provide more adsorption space for electrolyte ions, thereby generating more electric double-layer capacitance, mesopores can give a low-resistance transportation channel for adsorbing electrolyte ions to the surface of micropores, and macropores can store a certain amount of electrolyte ions, thereby shortening the transport distance of electrolyte ions.19 As a result, for electrode materials, porous carbon with abundant micropores is not a perfect candidate.

An ideal carbon electrode material with enough micropores for energy storage, enough mesopores for transporting ions, and a suitable amount of macropores for storing ions has long

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been highly desirable, which can not only ensure the efficient transport of electrolyte ions in channels but also maximize the specific capacitance of carbon-based supercapacitors. Of note is that porous carbons prepared by KOH or gaseous activation possess developed pore structures, which can provide sufficient specific surface area for electrolyte ions.20 However, these porous carbons have high microporosity, small pore size, and underdeveloped connectivity, which severely inhibit the effective transport of electrolyte ions in pore structures. To meet these requirements, a lot of studies have been focused on the template-assisted process.21 Although the template-assisted process can effectively generate narrowly distributed mesopores or even uniform macropores, its application is limited by complicated template preparation and subsequent removal.21,22 Consequently, there is an urgent need to find a strategy to maintain the natural texture properties of precursors simultaneously achieve elevated specific surface area.

Lignin is a resource-rich and renewable raw material.23,24 Unfortunately, most of the lignin during the paper-making process is wasted and leads to water pollution. More importantly, lignin has some natural porosity.25,26 Hence, the added value of lignin can be achieved by converting it into porous carbon. According to these results, a novel strategy is reported for holding the electrochemical attraction natural texture properties of the precursors and creating pores using a hydrothermal, KOH-assisted synthesis of lignin-derived porous carbon, of which bulk micropores provide a higher specific surface area for adsorbing ions, a lot of mesopores enhance the transport of ions, and bulk macropores serve as ion-buffering reservoirs. The as-formed PC-1 (3559.45 m\(^2\)/g) endows a high specific capacitance (i.e., 288.75 F/g at 0.5 A/g), excellent capacitance retention, and remarkable conductivity in a three-electrode system. This investigation offers a handy method to construct a novel carbon-based material by maintaining the excellent texture properties of the precursor while creating pores.

2. EXPERIMENTAL SECTION

2.1. Synthesis of PC-0 and PC-1. Lignin, employed as the raw material for the synthesis experiment, was obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. The lignin (5 g) and deionized water (60 mL) were put into an autoclave and then heated in a muffle furnace at 220 °C for 2 h to obtain a porous carbon precursor (PCP). After that, a mixture of PCP and KOH (10 g) was added to a nickel boat and then heated to 900 °C for 1.5 h in a tube furnace with a N\(_2\) atmosphere. The heating rate was 10 °C/min. PC-1 was collected for further experiment after cooling down. Besides, the synthesis process of PC-0 was the same as that of PC-1 except for the hydrothermal-assisted method.

2.2. Material Characterization. The specific surface area of PC-0 and PC-1 was calculated by the Brunauer–Emmett–Teller (BET) equation of \(N_2\) adsorption, while the pore size distribution was measured by nonlocal density functional theory (NLDFT). To observe the micromorphology of samples, scanning electron microscopy (SEM, FEI Inspect) and high-resolution transmission electron microscopy (HRTEM, JEOL-2100, JEOL Ltd.) were used. X-ray photoelectron spectroscopy (XPS, AXIS UltraDLD, Shimadzu) was used to analyze the surface element content of samples.

2.3. Electrochemical Test. The working electrode consists of carbon black, polytetrafluoroethylene, and PC-0 or PC-1 in a weight ratio of 1:1:8 and alcohol as a solvent. The slurry mixture was then coated onto nickel foam (100 mm\(^2\)) and vacuum-dried at 60 °C for 10 h. Finally, an electrode was manufactured by applying a pressure of 10 MPa. A three-electrode system with 6 mol/L KOH electrolyte was used for the electrochemical test. Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) were evaluated using an electrochemical workstation (CHI 660E, Shanghai Chenhua, China). The formula for calculating specific capacitance is given below.

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

where \(C\) (F/g), \(I\) (A), and \(\Delta t\) (s) stand for the specific capacitance, discharge current, and discharge time, respectively. \(\Delta V\) (V) and \(m\) (g) represent the potential window and weight of samples on the working electrode, respectively.

3. RESULTS AND DISCUSSION

3.1. Microstructure. 3.1.1. Texture Properties of PC-0 and PC-1. 6KOH + 2C \(\rightarrow\) 2K + 3H\(_2\) + 2K\(_2\)CO\(_3\) is the most common chemical activation for generating porous carbons.27,28 As is known, the texture properties of porous carbon can be obtained from \(N_2\) adsorption and desorption curves. For porous carbon with rich pore structures, the \(N_2\) adsorption and desorption curves usually consist of low-pressure, moderate-pressure, and high-pressure ranges. In the low-pressure range, the micropores are filled, which means that there is a multitude of micropores in samples. Curves with a hysteresis loop upon moderate pressure indicate the existence of mesopores in samples. In the high-pressure range, the curves rise sharply, meaning that there are macropores in samples.
The porosity hierarchy structures of PC-0 and PC-1 are depicted in Figure 1a.

In the low-pressure range, PC-0 and PC-1 possess a high slope of N2 adsorption and desorption curves, indicating that PC-0 and PC-1 have abundant micropores. However, compared with PC-0, PC-1 has relatively more micropores.

At a moderate pressure, compared with PC-0, the N2 adsorption and desorption curves of PC-1 have the smoothest change and are accompanied by the broad hysteresis loop. Consequently, PC-1 possesses a higher mesopore volume (Vmeso) and mesopore-specific surface area. Equally, in the high-pressure range, the N2 adsorption and desorption curves of PC-1 exhibit an upward trend, indicating that PC-1 endows macropores. For PC-1, this mentioned phenomenon confirmed its micro/meso/macropore hierarchical properties. To obtain the texture properties of PC-0 and PC-1, N2 adsorption and desorption curves were analyzed, as shown in Table 1.

PC-1 has the highest specific surface area (S\text{BET} = 3559.45 m^2/g), followed by ACDS4800 (S\text{BET} = 2609.00 m^2/g), PC-0 (2129.88 m^2/g), APFC–DES-40% (1238.81 m^2/g), PFC–DES-40% (596.81 m^2/g), and lignin (15.15 m^2/g). Zhang and co-workers reported a porous carbon with a specific surface area of 1672 m^2/g using KOH activation.30 Montane et al.12 obtained lignin-derived porous carbon (~1000 m^2/g) via H3PO4 activation. Of note is that the specific surface area of the reported porous carbons is significantly lower than those of PC-0 and PC-1. Moreover, the microporosities of APFC–DES-40%, PFC–DES-40%, ACDS4800, and PC-0 are all higher than 63.64%, suggesting that these porous carbons had developed micropores. This conclusion is consistent with previously reported studies.14–17 In sharp contrast, PC-1 has the lowest microporosity (21.49%) and is close to that of its precursor (lignin). For porosity higher than 2 nm, the data of PC-1 and its precursor (lignin) are relatively high and intensely close. As a result, the porosity of PC-1 retains most of the porosity of the precursor (lignin) without significant changes. Different from the precursor (lignin), PC-1 possesses the highest specific surface area (3559.45 m^2/g). These results confirmed that the hydrothermal, KOH-assisted process can create pores and simultaneously maintain the natural texture properties of lignin. Since PC-0 and PC-1 have a high specific surface area, they hold a promising application in many fields such as adsorption and catalysis.

To further understand the texture properties of PC-0 and PC-1, the pore size distribution is depicted in Figure 1b. Compared with PC-0, PC-1 possesses a relatively minor

| samples         | specific surface area (m^2/g) | micropore specific surface area (m^2/g) | V\text{micro} | V\text{meso} | V\text{macro} | porosity greater than 2 nm (%) | microporosity (%) | reference        |
|-----------------|-------------------------------|------------------------------------------|---------------|--------------|--------------|-------------------------------|-------------------|------------------|
| PC –0           | 2129.88                       | 1631.40                                  | 1.103         | 0.726        | 0.163        | 34.18                         | 65.82             | this work        |
| PC –1           | 3559.45                       | 1135.17                                  | 2.313         | 0.497        | 1.267        | 78.51                         | 21.49             |                  |
| APFC–DES-40%    | 1238.81                       | 1152.24                                  | 0.534         | 0.462        | n.d          | 13.48                         | 86.52             |                  |
| ACDS4800        | 2609.00                       | 1825.00                                  | 1.100         | 0.700        | n.d          | 36.36                         | 63.64             |                  |
| lignin          | 15.15                         | n.d                                      | 0.017         | 0.016        | n.d          | 100                           | n.d               | this work        |
| PFC–DES-40%     | 596.81                        | 528.53                                   | 0.289         | 0.208        | n.d          | 28.03                         | 71.97             | 16,29            |

**Table 1. Texture Properties of Lignin, PCs, and Other Porous Carbons Reported in the Literature**

"PFC–DES-40%, APFC–EDS-40%, and ACDS4800 represent the porous carbon derived from phenolic resin one-time activation, the porous carbon derived from phenolic resin two-time activation, and the date seed-derived porous carbon, respectively. Data that could not be found are marked with n.d in this work.

Figure 2. SEM image (a) and HRTEM image (b) of PC-1; SEM images of lignin (c) and PCP (d).
amount of pore size distribution within the range of 1.13−1.23 nm. Notably, PC-1 possesses a majority of pore size distribution at 0.75−1.13 nm and 1.23−5 nm. Interestingly, porous materials rich in 2−5 nm are beneficial for removing dioxins.32 In other words, PC-1 equally holds a promising application for adsorption dioxins. According to the literature, porous carbons with high specific surface area hold an up-and-coming application in supercapacitors.33,34 Deng and co-workers utilized phenolic resin-derived porous carbon (∼1085.25 m²/g) as the electrode material for capacitors.16 Equally, the application of rice straw-derived porous carbon (∼1007 m²/g) for the electrode material of supercapacitors has been recorded in the work of Sudhan and co-workers.35 Notably, the specific surface area of the mentioned porous carbons is much lower than those of PC-1 and PC-0, especially PC-1. In reviewing the literature, the pore structure with a pore size of 0.4−1 nm can provide a good adsorption area for the adsorption of electrolyte ions, while a pore size greater than 2 nm can give an efficient channel for transporting electrolyte ions.36 Although APFC−DES-40%, ACDS4800, and PC-0 have sufficient micropores for energy storage, there is no proper amount of pore size greater than 2 nm for transporting. Compared with porous carbon, PC-1 possesses several advantages, including but not limited to the ultrahigh specific surface area (3559.45 m²/g), appropriate micropore specific surface area (1135.17 m²/g), appropriate V_meso (0.575 cm³/g), and suitable V_macro (1.267 cm³/g). Accordingly, PC-1 has a promising application as an electrode material for high-performance supercapacitors.

3.1.2. Microscopic Morphology of Samples. To reveal the microscopic morphology of samples more intuitively, SEM and HRTEM tests were carried out. Figure 2a evidences a honeycomb-like surface, illustrating that PC-1 has an enriched porosity, which is consistent with the result of its ultrahigh specific surface area. Similarly, the presence of narrow pores in wide pores is depicted in Figure 2a, and nanopores are observed in Figure 2b. The mean PC-1 possesses hierarchical structures. Besides, a 3D architecture with hierarchical structures is clearly revealed in Figure 2a,b. The pore structures are graphitized, resulting from the higher activation temperature (900 °C). The microscopic morphology of as-formed PC-1 is not only consistent with and more intuitive than the results of its N₂ adsorption/desorption curves.

To further understand the reason for creating more porosity while maintaining the natural texture properties of lignin, lignin and PCP were tested using SEM. Due to the limitation of the experiment, the surface of lignin is relatively complete and there is almost no pore structure, as exhibited in Figure 2c. It is worth mentioning that there are some pores on the surface of PCP, as shown in Figure 2d, which is results from the depolymerization of part structures for lignin. The depolymerization mechanism will be further investigated after this work. These results suggest that the hydrothermal-assisted method
results in the formation of initial pore structures for PCP, which played a crucial role in the directional development of PC-1 during the subsequent activation of PCP.

3.2. Nature of PC. Porous carbons doped with N/P/S can further enhance their electrochemical properties that have been recorded in previous studies.37−39 As a result, XPS was applied for determining the element content on the surface of PC-1. It can be seen from Figure 3a that there are a large amount of C and O elements on the surface of PC-1, and there is an exceedingly small amount of S (as listed in Table 2).

Here, coconut shell activated carbon was named AC. MnO2-AC represents MnO2-loaded AC.

Table 2 shows that the contents of C and O on the surface of PC-1, AC, and MnO2-AC are relatively close. Besides, the order of PC-1 surface element contents was determined: C > O > S. The C 1s spectra of PC-1 are exhibited in Figure 3b; the sharp C 1s peak at ~284.7 eV is attributed to the C−C/C=C bond, which can be assigned to sp2 graphite crystal. Moreover, the peaks at ~286, ~287.1, and ~289 eV are attributed to the C−O, C=O, and O−C=O bonds, respectively, and their contents are listed in Table 2. According to these results, it is concluded that the as-obtained PC-1 is the primary sp2-hybridized carbon. Furthermore, the deconvolution of O 1s spectra (Figure 3c) suggests four O-containing functional groups, namely, C=O (531.10 eV), C−O/C−OH (532.80 eV), C−O−C (533.70 eV), and O−C−O (534.40 eV). The O-containing functional groups can effectively improve the wettability between electrolytes and electrode materials. Similarly, the deconvolution of S 2p spectra (Figure 3d) indicates three S-containing functional groups, including C−S−C (164.23 eV), −C=S− (165.33 eV), and C=S=O−C (169.33 eV). Luo et al.40 obtained chitosan-based hydrogen-derived porous carbon with an N content of 4.9% and indicated that it had a limited pseudocapacitance. Verma et al.41 reported a N (~1.35%) and S (~0.85%) co-doped porous material and illustrated that it has a limited pseudocapacitance.

Figure 4. GCD curves of PC-0 (a) and PC-1 (b) at different current densities. (c) GCD curves of PC-0 and PC-1 at 0.5 A/g; CV curves of PC-0 (d) and PC-1 (e). (f) Nyquist plots of PC-0 and PC-1 in 6.0 M KOH, recorded at frequencies ranging from 0.01 to 100 kHz.
Compared with the mentioned works, the S content of the surface of PC-1 was intensely low (0.06%). Meanwhile, N and P elements on the surface of PC-1 were hardly found, which is consistent with the preparation approach of this study. Consequently, in the following discussion, S, P, and N doping was not discussed if not mentioned otherwise. Compared with other porous materials reported in the literature, there are a relatively few functional groups on the surface of PC-1, which is conducive to the following analysis and discussion.

### 3.3. Electrochemical Performance

Specific capacitance is one of the most crucial performance indicators of supercapacitors. Consequently, the electrochemical work-station was applied to GCD measurement. The GCD curves of PC-0 and PC-1 upon different current densities are demonstrated in Figure 4a,b. Besides, the GCD curves of PC-0 and PC-1 upon 0.5 A/g are exhibited in Figure 4c.

As is known, isosceles triangles are apparent in GCD curves, suggesting ideal double-layer capacitor behaviors. Accordingly, PC-0 and PC-1 have outstanding double-layer capacitor behaviors, especially PC-1. Compared with PC-0, the charge/discharge time and charge storage capacity of PC-1 are significantly increased. Furthermore, a little sudden voltage drop in the GCD curve of PC-1 was observed during supercapacitor charging and discharging conversion. Therefore, its equivalent series resistance ($R_s$) is low.

Table 3 presents the specific capacitances of PC-0 and PC-1, and their corresponding broken-line graph is denoted in Figure 5.

**Figure 5. Change plot of specific capacitance.**

Evidently, the specific capacitance of PC-1 was significantly higher than that of PC-0 because PC-1 has a developed hierarchical pore structure, a high specific surface area (3559.45 m$^2$/g), and a low microporosity (21.49%). Besides, the specific capacitance of PC-1 is higher than that of the best reported biomass-derived porous carbons (as listed in Table 4) and the commercially available supercapacitors.

With an increase in the current density, the specific capacitance gradually decreased. As an example, the specific capacitance of PC-1 decreased from 288.75 F/g at 0.50 A/g to 223.72 F/g at 10.00 A/g. This conclusion is consistent with that of previous studies. Furthermore, the capacitance retention of PC-1 was relatively high, up to 77.48% at 10 A/g, which is higher than those mentioned in previous studies (73% at 10 A/g, 53% at 10 A/g, 74% at 10 A/g, 64% at 10 A/g$^{53}$). This is because PC-1 has developed pore structures and high mesopore content, and there are benefits to capacitance retention. Upon reviewing the literature, the specific capacitance of PC-1 is much higher than that of straw-derived porous carbon (156 F/g at 0.50 A/g) and jute stick-derived porous carbon (162 F/g at 1 A/g). As a result, the hydrothermal, KOH-assisted method is an unprecedented approach to prepare porous carbon with elevated electrochemical properties.

**Figure 4d,e** depicts the CV curves of PC-0 and PC-1 at the scan rate range of 5–100 mV/s. Upon reviewing the literature, a rectangle-like CV curve suggests that electrolyte ions can diffuse into micropores within a sufficient time. In other words, the reversibility of charging and discharging is better. Thus, PC-0 and PC-1 possess a better charge/discharge reversibility within a scan rate range of 5–50 mV/s. As is known, the micropores have the highest resistance, followed by mesopores and macropores. Consequently, with an increase in the scan rate, the degree of rectangularity for CV curves increasingly decreases. Notably, redox peaks in CV curves for PC-0 and PC-1 were not found, indicating that they possess remarkable electrochemical stability.

To further evaluate the electrochemical properties of PC-0 and PC-1, EIS tests were performed. Generally, the EIS Nyquist chart consists of low-frequency, mid-frequency, and high-frequency regions. Among them, the high-frequency region represents the charge transfer resistance of the electrolyte/active material interface. The low-frequency region indicates the charge diffusion-limited process. Moreover, the ($R_s$) values of PC-0 and PC-1 were 0.68 and 0.65, respectively, which are lower than many previous works (0.88, 0.78, 0.93, and 0.82 F/g$^{53}$). As a result, PC-1 as an electrode material possesses remarkably conductivity.

### Table 4. Chemical Activation Agent, Texture Property, and Specific Capacitance of Biomass-Derived Porous Carbons Reported in the Literature

| Biomass            | Chemical activation agent | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{mic}}$ / $V_{\text{total}}$ (%) | Test system electrode/electrolyte | Specific capacitance (F/g) |
|--------------------|---------------------------|-----------------------------|------------------------------------------|-----------------------------------|-----------------------------|
| Lignin [48]        | $\text{H}_3\text{PO}_4$  | 1474.82                     | 31.09                                    | 3E/6 M KOH                        | 154.50 (1 A/g)              |
| Jute stick [49]    | KOH                       | 949                         | 39.13                                    | 3E/6 M KOH                        | 173 (1 A/g)                 |
| Camellia petals [50]| (NH$_4$)$_2$S$_2$O$_8$     | 1122                        | 44.51                                    | 3E/6 M KOH                        | 78 (10 A/g)                 |
| Lignocellulosates [51]| H$_2$PO$_4$             | 1135                        | 3E/1 M Na$_2$SO$_4$                    | 165 (0.05 A/g)                    |
| Sulfonated pitch [52]| KOH                     | 2602                        | 34.38                                    | 3E/6 M KOH                        | 212 (5 A/g)                 |
| This work (PC-1)   | KOH                       | 3559.45                     | 21.49                                    | 3E/6 M KOH                        | 288.75 (0.5 A/g)            |
while, PC-1 shows significant capacitance performance, resulting from the high slope in the low-frequency region. Given its environment friendliness, low cost, and excellent capacitance, PC-1 would possess a promising application as a candidate material for the next generation of high-performance supercapacitors.

4. CONCLUSIONS

In summary, this work presents a novel approach for maintaining electrochemical attraction natural texture properties of precursor and creating pores. Employing this feasible method, a 3D architecture with hierarchical structure porous carbon accompanied by ultrahigh specific surface area (3559.45 m²/g) can be obtained. Compared with common porous carbons, PC-1 possesses several advantages, including but not limited to the ultrahigh specific surface area, appropriate micropore specific area, appropriate \( V_{mic} \) and suitable \( V_{mac} \). Benefiting from these texture properties, PC-1 achieves a high specific capacitance of 288.75 F/g at 0.5 A/g, excellent rate capability, and admirable conductivity. Considering its environment friendliness, low cost, and excellent capacitance, this handy approach to synthesize unique structure porous carbon for high-performance supercapacitors is feasible.

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Notes
The authors declare no competing financial interest.

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