Short Communication

Hierarchical porous carbon prepared from biomass through a facile method for supercapacitor applications

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GRAPHICAL ABSTRACT

A general method has been developed to prepare angstrom-sized-pore dominated hierarchical porous carbon from biomass for supercapacitor applications.
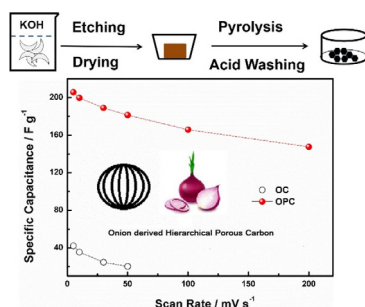
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ABSTRACT

The porous carbon with angstrom-sized pores is important in supercapacitor applications, because of its high pack density and high specific capacitance. In this paper, a facile method is proposed for the preparation of hierarchical porous carbon with high-volume angstrom-sized pores. Onion, as the typical biomass in this research, is used as carbon precursor. First, onion was etched by KOH to obtain a water-soluble lignin-potassium-salt/cellulose composite. This composite was further pyrolyzed under N_2 atmosphere to obtain onion derived porous carbon (OPC). The morphology and porous structure of OPC were characterized by scanning electron microscope and N_2 adsorption/desorption. The supercapacitive performances of OPC were investigated by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge-discharge. OPC shows high specific surface area with high-volume angstrom-sized pores in carbon matrix. When used as supercapacitor electrode materials, OPC shows high specific capacitance and good cycling stability. This paper opens a general way to prepare porous carbon from biomasses, which will promote the development of biomass utilization, preparation of porous carbon and supercapacitors.

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1. Introduction

The past decades have witnessed great progress in the research and development of supercapacitors. Nowadays, supercapacitors are widely used in various applications, such as electric vehicles, uninterruptible power supply, and electronics. Supercapacitor mainly refers to electric double layer capacitor (EDLC) using porous carbon as electrode materials. Although has been a commercial product for many years, supercapacitor still faces the drawbacks of low energy density and the high cost of porous carbon [1]. The performances of supercapacitor can be enhanced through the preparation of hierarchical porous carbon. Hierarchical porous carbon usually contains inter-connected micropores, mesopores, and macropores. Micropores provide the effective electrode/electrolyte interface for the construction of electric double layer capacitor and mesoporous channels facilitate the electrolyte diffusion [2]. Although have little impact on the increase of specific capacitance, macropores act as electrolyte reservoir for shortening the distance of ion diffusion [3].

Hierarchical porous carbon materials are usually prepared through combined template/activation method [4–6]. Template process consumes large amount of inorganic or organic template and the preparation procedures of templates are complicated. Activation can provide porous carbon with high surface area but consumes large amount of activation agents, such as KOH and NaOH. Simplifying complex traditional template-assisted carbonization-activation process relies on simplifying the procedures or eliminating activation agent. Direct carbonization/pyrolysis method has been extensively studied due to the facile processes and the elimination of using activation agent [7–18]. In these researches, seaweeds [7], potassium citrate [8], copolymer [9], MOFs [10], and some metal organic salts [11,12] have been used as carbon precursors. A newly developed direct pyrolysis method designed by Ji et al. is self-activation, where cellulose was activated by the pyrolysis gases [13]. This method has a general meaning that most organics can be transformed into porous carbons using self-activation. As mentioned above, most direct pyrolysis strategies applied organic salts as carbon precursors [14–18]. When considering advantages, direct pyrolysis method also avoids the mass transfer of KOH in carbon matrix in traditional activation process [19]. Also, by choosing appropriate carbon precursors, very narrow pore distribution can be obtained [20]. Recently, a study explores the synthesis of angstrom-sized porous carbon by direct pyrolyzing of hydrothermally treated precursor, by choosing the alkali with different metal ions, one can precisely control the pore size [21]. Angstrom-sized porous carbon can increase specific capacitance, hence the preparation of hierarchical porous carbon with high volume of angstrom-sized pores is very important.

During the past 3 years, our group has been exploring simple preparation methods for porous carbon materials from a general biomass, such as lignin [22,23] and rice husk [1]. The advantage of biomass over petroleum-based chemicals is its renewability and sustainability. *Allium cepa*, usually called onion, is probably
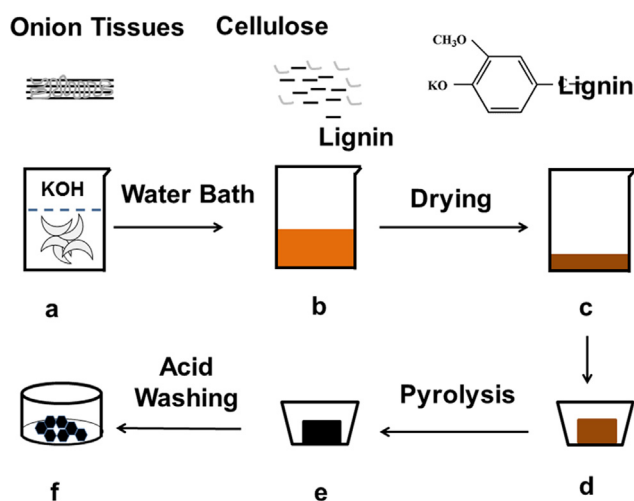

Fig. 1. Schematic diagram of the formation processes of OPC. (a) Onion flakes immersed in KOH solution at 95 °C. (b) KOH etched onion forming brown slurry. (c) The brown slurry was dried for 72 h at 100 °C to turn into a brown solid. (d) The brown solid was scribed to form particles. (e) The brown particles were pyrolyzed at 900 °C. (f) The pyrolysis product was washed with HCl and deionized water to form porous carbon. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
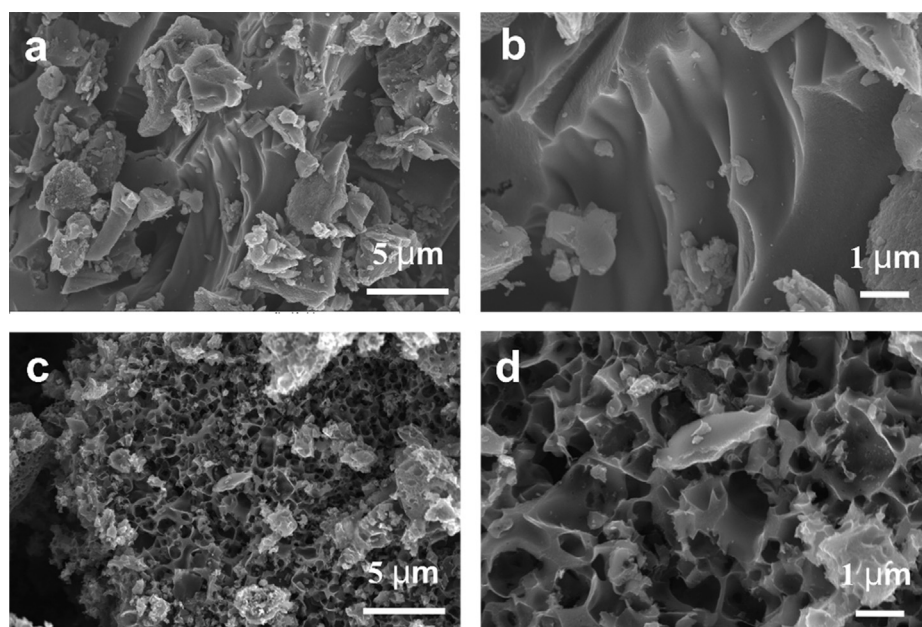

Fig. 2. (a and b) SEM image of OC; (c and d) SEM image of OPC.

the most widespread vegetable in the world [24], with a production of approximate 150 million tones one year. Wang et al. prepared a unique hierarchical porous carbon from onion for supercapacitor applications [24]. By using onion as a typical biomass, we have developed a general and simple way to prepare hierarchical porous carbon from biomass.

In this paper, after etching onion with KOH, a facile direct pyrolysis method has been proposed to prepare hierarchical porous carbon (onion derived porous carbon, OPC) with high-volume angstrom-sized pores to be used in supercapacitor applications. OPC shows high capacitance, good rate performance, and high stability. More importantly, this general method can be further applied in other biomasses.

2. Experimental section

2.1. Preparation of OPC

Allium cepa (Onion) was bought from the campus market of Jilin University. KOH and HCl bought from Beijing Chemical Works were of analytical grade. Onions were washed with water to remove dusts and soluble impurities and then, onions were cut into small flakes with the size of centimeters. For the preparation of onion derived porous carbon (OPC), 100 g onion flakes were put into 600 mL KOH solution containing 4 g dissolved KOH. The above solution was magnetically stirred at 1000 rpm for 10 h with a heating temperature of 95 °C, the solution was then transformed into slurry. The obtained slurry was dried from 48 h at 100 °C to get a black solid. Subsequently, the solid was direct pyrolyzed at 900 °C in a tubular furnace for 1 h under N_2 atmosphere. Finally, the obtained pyrolysis product was washed with 10 wt% HCl with stir stirring for 10 h and washed by deionized water to neutral pH respectively. The obtained carbon materials was dried at 120 °C for 24 h. Onion derived carbon (OC) was prepared by pyrolyzing dehydrated onion (heat treated for 72 h at 100 °C) under the same heat treatment program as OPC. All the chemicals in this study were of analytical grades and water used in this experiment was deionized water.

2.2. Physical characterization

N_2 adsorption–desorption analysis was tested by using a specific surface analyzer (3H-2000PM2, Beishide, Beijing, China). Surface area was analyzed by Brunauer–Emmett–Teller (BET) model. The micropore size distribution was calculated by Horvaih–Kawazoe (HK) method. Mesopores size distribution was calculated by Barrett–Joyner–Halenda (BJH) method. Scanning electron microscope (Merlin-61-95, ZEISS, Germany) was used to characterize the surface morphology of obtained carbon materials. Raman spectroscopy was measured on a micro-Raman spectrometer (LabRAM ARAMIS, Horiba-Jobin Yvon) with notch filters cutting at 100 cm^{-1} using a Cobalt laser (473 nm, 5 mW at the source). X-Ray Diffraction (XRD) patterns were taken on a Bruker diffractometer (D8 Advance) with Cu Ka radiation, λ = 0.5406 Å at a scan rate of 5° min^{-1}.

2.3. Electrochemical measurement

The electrode was composed of OPC or OC, acetylene black and PTEE with mass ratio of 8:1:1. The electrode was cut into small rectangular films with geometric surface of 1 cm × 1 cm and loaded on foamed nickel at 15 Mpa for 5 min. Areal mass loading of carbon was approximately 3.5 mg cm^{-2}. Symmetric supercapacitor was assembled into CR3023 coin cells with 6 M KOH electrolyte. An electrochemical workstation (PMC-1000, Princeton

Applied Research, USA) was used to analyze cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). A battery tester (BTS-4008 5 V/50 mA, Neware, China) was used to perform galvanostatic charge–discharge (GCD) test. All the calculations are based on our previous paper [22,23].

3. Result and discussion

Direct pyrolysis approach usually uses organic salt as carbon precursor. Metal ions in the organic framework will be transformed into porogen (metal, metal oxides or metal carbonate), when washed away porogen, porous structure will leave in carbon matrix.
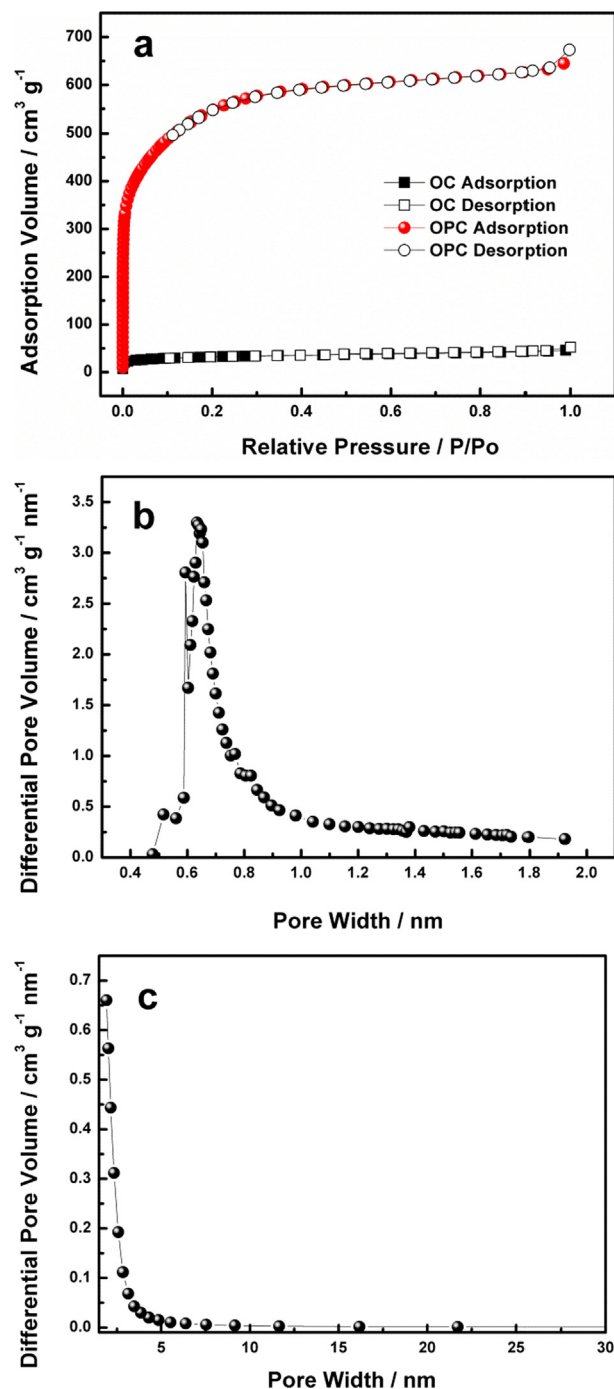

Fig. 3. (a) N_2 adsorption-desorption isotherms of OPC and OC; (b) micropore size distribution of OPC; (c) mesopore size distribution of OPC.

Metal ions, such as K, Na, and Zn behaves like activation agent, and the carbon skeleton will be etched by K, Na and Zn species [25,26]. The direct pyrolysis of organic salts is simple compared with carbonization-activation method. However, this method can be applied only to organic salts, metal-intercalated organics, and MOFs. Herein, we have developed a general method to prepare porous carbon from general biomasses. Onion with soft cellulose (~41%), hemicellulose (~16%), lignin (~39%) and extractive (~4%) components was chosen as the typical carbon precursor in our research. The component of onion is similar to most biomasses, so the method proposed in this paper should be easily developed to prepare porous carbons derived from other biomasses.

The procedures to prepare onion-derived porous carbon are displayed in Fig. 1. Onion flakes can't be dissolved in water (See Supporting Information, Fig. S1), since original cellulose and lignin in biomasses are cross-linked together. However, with KOH etching, onion flakes can be gradually dissolved in water (Fig. S2). In this process, KOH breaks the chemical bond between hemicellulose molecules and lignin. The cellulose in onion is soft, maybe is of low molecule amount. So it can be easily broken into small fibers in water through breaking the hydrogen bond between cellulose molecules. In case of the lignin component, the large amount of phenolic hydroxyl groups react with KOH forming lignin potassium salt. After KOH etching, onion was transformed into lignin-potassium-salt/cellulose (hemicellulose) composite. When the composite solution was dried, the slurry turns into black solids (Fig. S3b). These black solids can be dissolved totally in water (Fig. S4) because cellulose is of small molecular weight, and lignin potassium salt and hemicellulose are water-soluble. The obtained black solid was transferred to pyrolysis process. After pyrolysis and acid washing, onion derived porous carbon (OPC) is obtained (Fig. S3d).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.06.076.

Onion derived carbon (OC) is micron-sized particle with small particle scattered around OC (Fig. 2a and b). OPC has 3D inter-connected macroporous channel (Fig. 2c and d). The 3D connected macroporous channels with thin carbon walls (Fig. S5) are

Table 1
Pore parameters of OPC and OC.

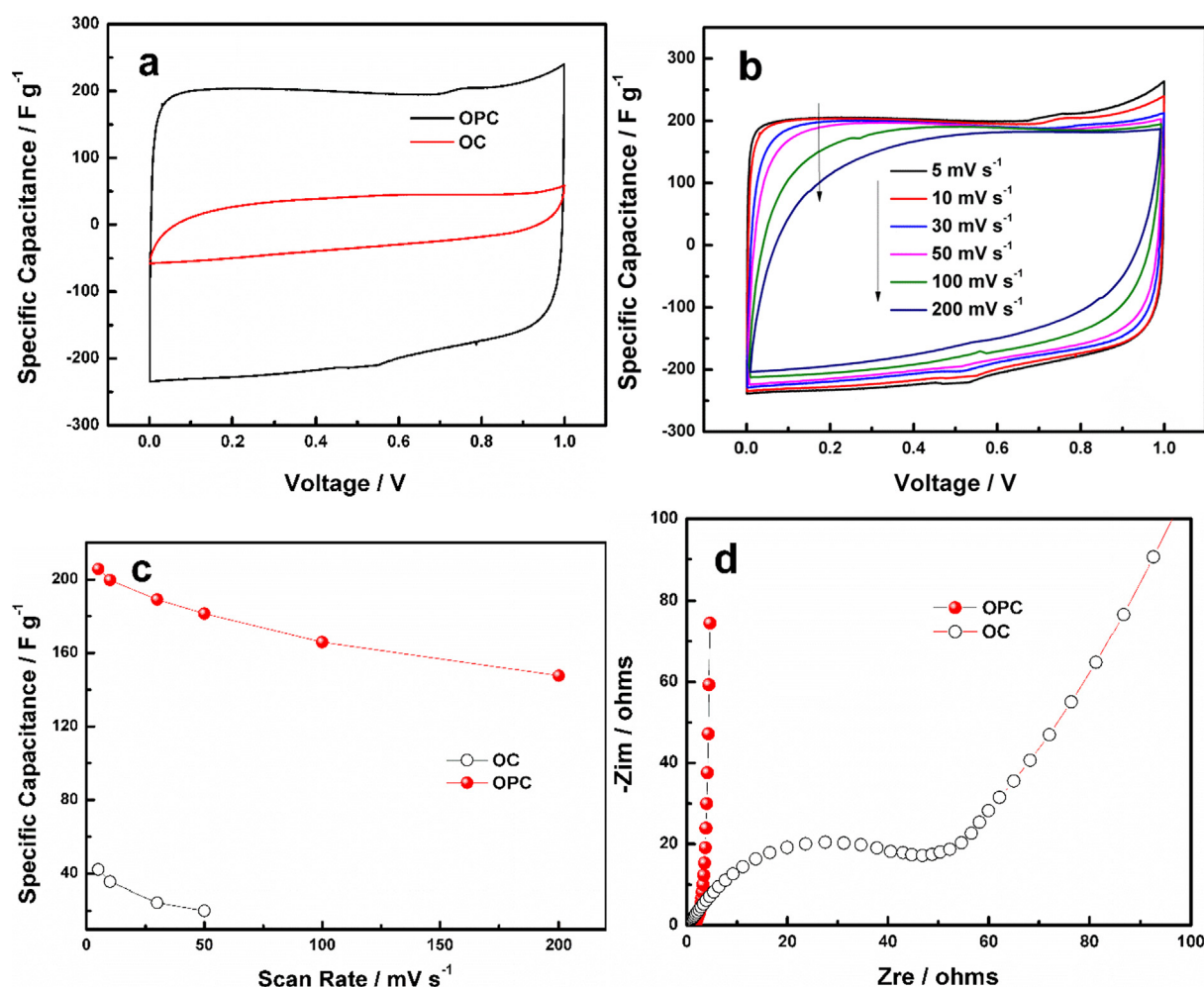| Samples	S_{BET} (m^2 g^{-1})	$S_{t\text{-plots}}$ (m^2 g^{-1})	V_{micro}/V_{total} (%)	V_{total} (cm^3 g^{-1})	V_{micro} (cm^3 g^{-1})	$S_{t\text{-plots}}/S_{BET}$ (%)
OC	116.4	90.300	57.4	0.0804	0.0461	77.6
OPC	1914.9	1760.8	74.9	1.0412	0.7798	91.9

Fig. 4. (a) Cyclic voltammograms of OC and OPC at 5 mV s^{-1}. (b) Cyclic voltammograms of OPC at scan rates from 5 to 200 mV s^{-1}. (c) Dependence of specific capacitance on the scan rate. (d) Nyquist plots of OC and OPC based symmetric supercapacitor at 0 V.

mainly caused by the evolution of gases when lignin is degraded during pyrolysis [27]. The 3D macroporous channels could help OPC build up a hierarchical porous structure which is beneficial for electrolyte diffusion.

Like most of biomass-derived carbon materials [28–31], OC and OPC are both of amorphous structure, which is identified from XRD patterns (Fig. S6) and Raman spectra (Fig. S7). XRD shows two humps at 25° and 44° demonstrating the amorphous characteristic of OPC. The huge D peak in Raman spectra indicates that there are numerous defects exist in OC and OPC. The lignin potassium organic salts formed during KOH etching process are transformed into porous carbon in the pyrolysis process. N_2 adsorption-desorption was used to identify the porous structure of OPC (Fig. 3). OPC shows typical type I isotherm (Fig. 3a), which means that large amount of micropores exist in OPC. OPC shows a very narrow micropore distribution with a peak centered at 0.7 nm (Fig. 3b). The existence of angstrom-sized pores below 1 nm is good for the enlargement of capacitance. Mesopore distribution is obtained by BJH method. There is a very low volume of meso-pores above 2 nm (Fig. 3c). The co-existence of micropore, meso-pore, and macropore channels offer a typical 3D hierarchical porous structure. The macropores act as electrolyte reservoir of particle-packed thin film electrode [3]. The mesopores enhance the mass transfer and micropores further enhance the specific capacitance. OC shows a small specific surface area of 116.4 m^2 g^{-1}, which is a typical specific surface area of carbonized organics.

On the contrary, OPC shows a specific surface area as high as 1914.9 m^2 g^{-1} with a microporous surface area of 1760.8 m^2 g^{-1} and a surface area ratio of 91.9% (Table 1), which demonstrates that most surface area originates from the micropores. It is inter-esting that most of the present pores are micropores. The micropore-dominated pore structure is attributed to the steric hindrance effect since potassium ions affiliated to lignin are homo-geneously distributed and separated by the large lignin molecule in the pyrolysis process resulting in the limited space for the potassium self-activation. The angstrom-sized micropores have shown a beneficial effect on the construction of EDLC [19,20], hence, angstrom-sized microporous carbon is attractive for super-capacitor applications. For example, Zhou et al. developed hydrothermal-carbonization method to prepare microporous car-bon from 2,4-dihydroxybenzoic acid, formaldehyde and alkali hydroxide [21]. Xu et al. developed a method to prepare microp-orous carbon from the pyrolysis of PVDF [32–34]. Compared with the above methods, our method is green, sustainable and has a general meaning that can be applied to most biomasses.

Electrochemical tests were carried out in a two-electrode sym-metric cell with the same mass loading on both positive and neg-ative electrodes. OPC shows higher specific capacitance compared with OC within the total voltage range (Fig. 4a). OPC shows an almost constant specific capacitance of 200 F g^{-1} in the positive scan direction as shown in Fig. 5a, while OC only shows a specific capacitance of ca. 50 F g^{-1}. With increasing scan rate, OPC behaves
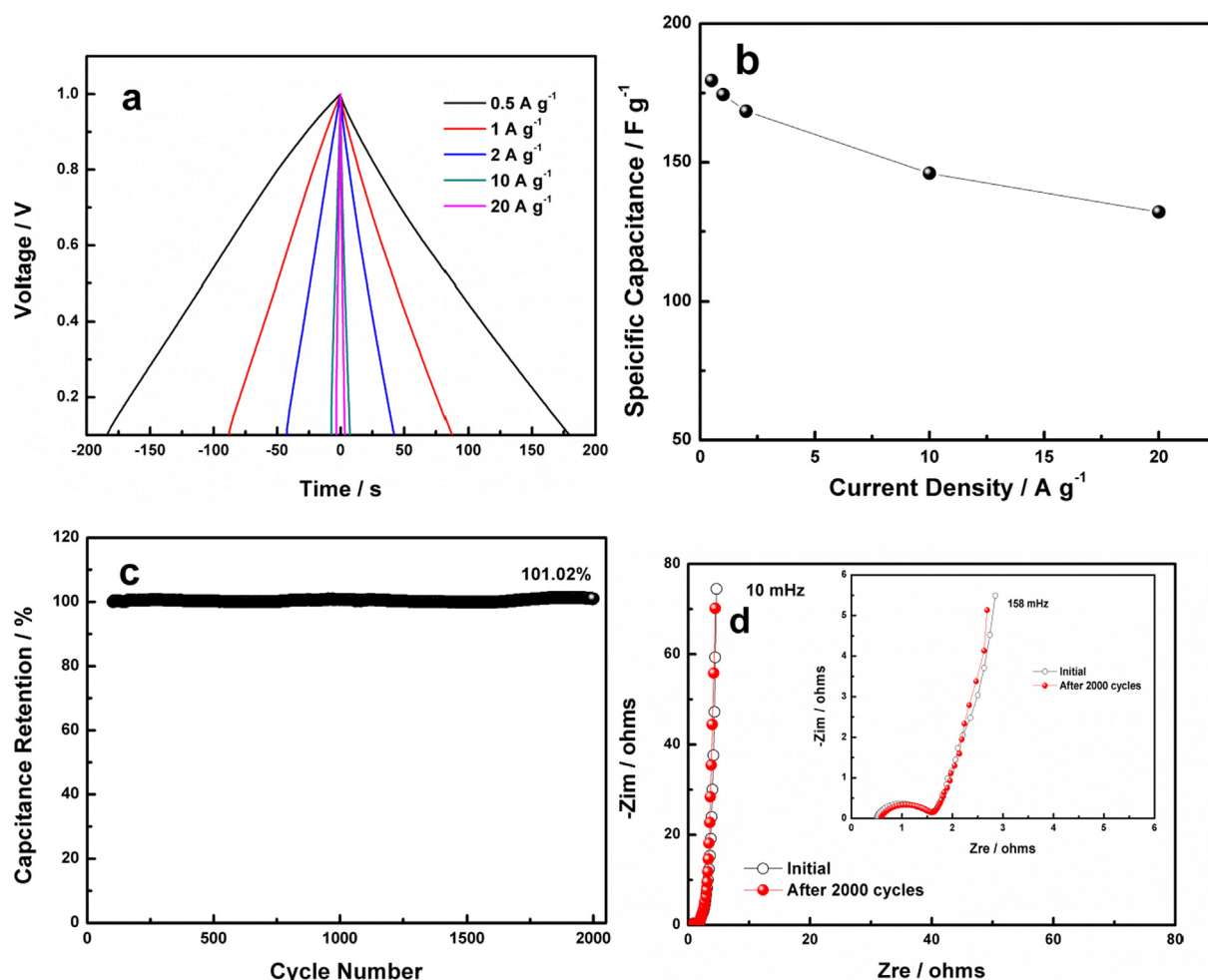

Fig. 5. (a) GCD curves of OPC from current density of 0.5 A g^{-1} to 20 A g^{-1} in 6 M KOH electrolyte. (b) Dependence of the specific capacitance of OPC on GCD current densities ranging from 0.5 A g^{-1} to 20 A g^{-1}. (c) GCD cycling performance of OPC at 2.0 A g^{-1} in 6 M KOH electrolyte solution. (d) Nyquist plot of the OPC based symmetric supercapacitor before and after 2000 GCD cycles.

quasi-ideal capacitive behavior with symmetric rectangular shape in the scan rate from 5 mV s^{-1} to 200 mV s^{-1} (Fig. 4b). The rectangular shape of the cyclic voltammogram of OPC keeps well even at a high scan rate of 200 mV s^{-1}. Specific capacitances based on the CV results are displayed in Fig. 4c, with a scan rate of 5 mV s^{-1}, the specific capacitance of OPC is 205.7 F g^{-1}, while OC only has a small specific capacitance of 42.2 F g^{-1}. With the increase of scan rate to 200 mV s^{-1}, the specific capacitance of OPC still sustains at 147.7 F g^{-1}. Nyquist plot shows the different impedance behavior of OC and OPC (Fig. 4d). OC shows large semi-circle at high-frequency range due to the small EDLC capacitance and oxygen-function-groups dominated pseudocapacitance. OPC possesses high specific capacitance, hence, in the low-frequency range, OPC behaves like a pure capacitor.

Galvanostatic charge–discharge (GCD) tests were used to determine the specific capacitances with varied current densities (Fig. 5a). With the increase of current density, GCD of OPC shows triangular shapes indicating the quasi-ideal capacitive behavior of OPC. OPC has high specific capacitance when tested with GCD methods (Fig. 5b). OPC has a capacitance of 179.5 F g^{-1} at a current density of 0.5 A g^{-1}, while OPC still has a high specific capacitance of 132 F g^{-1} at a current density of 20 A g^{-1}. With the increase of current density, the voltage drop displays almost linear relationship with current density (Fig. S8). The internal resistance decreased with the increase of current density (Fig. S9), due to the decreased real impedance at high-frequency ranges.

OPC shows high stability with a capacitance retention of 101.2% for 2000 GCD cycles (Fig. 5c). The OPC also shows nearly unchanged Nyquist shape (Fig. 5d), with little change in the electrical parameters after cycling. Equivalent circuit in Fig. S10 was used to simulate the electrical parameters before and after GCD cycling (simulated data are shown in Table S1). The detailed description of electric elements is introduced in Fig. S10. Simulated Nyquist plots are shown in Fig. S11. After GCD cycling, the ohmic resistance changed from 0.4902 Ω cm^2 to 0.5849 Ω cm^2, and the diffusion resistance changed from 0.5805 Ω cm^2 to 0.6509 Ω cm^2. Slightly changed ohmic resistance and diffusion resistance demonstrate the stable behavior when OPC was used as electrode materials for supercapacitors. As a typical micropore-dominated hierarchical porous carbon, OPC shows comparable supercapacitive performance over other delicately designed microporous carbon materials (Table S2). What's more, the significance of the preparation method of OPC is that it is a simple and general way using biomass as carbon precursor to prepare porous carbon for supercapacitor applications.

4. Conclusion

In a summary, a facile method was developed to prepare hierarchical porous carbon with large volume angstrom-sized pores from biomasses. The major component of onion (cellulose, hemicellulose and lignin) can be dissolved in KOH solution due to the break of the chemical bond between cellulose molecules and the formation of lignin-potassium-salts/cellulose composite. The potassium sites of lignin potassium salts act as activation agent (porogen) in the carbonization process. The obtained onion derived porous carbon (OPC) has high specific surface area and high volume of angstrom-sized porosity. OPC shows superior performance in supercapacitor applications. From a general perspective, this facile and simple method should be developed to prepare porous carbon materials from other biomasses for emerging applications.

Acknowledgement

Conflict of interests

Authors declare no conflict of interests.

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