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Preparation of Activated Carbon Derived From Xanthoceras sorbifolium Bunge and its Electrochemical Properties

Ruiyao Yao[1,2], *Zhiqian Li*[1,2], *Hongli Gao*[1,2],*Guoying Wang*[1,2], *Gaofeng Shi*[1,2*]

[1] School of Petrochemical Engineering, Lanzhou University of Technology, Lan gong ping Road, Lanzhou, Gansu, China
[2] Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province
[*]E-mail: 971584796@qq.com

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Porous carbon was the reside of Xanthoceras sorbifolium Bunge oil after pressing as carbon source and zinc chloride as activator. Multistage porous carbon was prepared. The chemical and physical properties of porous carbon materials were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen adsorption/desorption, Raman spectroscopy and XPS. Nitrogen adsorption/desorption experiments show that $ZnCl_2$ has good pore expansion, with a total pore volume of 0.68 cm3/g and a maximum specific surface area of 1079.79 m2/g. At 1 A/g current density, the specific capacitance is 220 F/g. The results show that multistage carbon is one of the ideal electrode materials for supercapacitors.

Keywords: electrochemical properties; xanthoceras sorbifolia; porous carbon

1. INTRODUCTION

People's consumption of energy is increasing day by day with the rapid improvement of human living standard. Development of green and sustainable new energy is imminent. Among various kinds of energy storage device, the supercapacitors(SCs) represents a super advanced electrochemical energy storage technology[1]. SCs have the advantages of fast charge and discharge, long cycle life, strong anti-interference, flexible operation, also have the remarkable energy storage potential[2,3]. SCs combine the advantages of both traditional capacitors and batteries, so it is necessary to develop excellent electrode materials for SCs[4].

Xanthoceras sorbifolium bunge is a unique woody oil plant in China, with high industrial value and nutritional value. This oil contains a special kind of material - nervonic acid, can recovery of cerebral nerve function and has been in the market now senior Xanthoceras sorbifolium Bunge oil on sale[5]. In 2020, the government included Xanthoceras sorbifolium Bunge into the *Catalogue of Tree Species for National Reserve Forest*, and the country vigorously promoted the planting of this tree species to expand the planting area of Xanthoceras sorbifolium Bunge[6]. In addition, xanthocorpa sorbifolium bunge oil contains free fatty acids. xanthocorpa sorbifolium bunge oil is an perfect resource for the production of biodiesel[7,8]. In order to obtain diesel oil, a large amount of Xanthoceras sorbifolium Bunge residue was produced, which not only increases the burden of garbage disposal, but also causes the depreciation of resources. Therefore, it is necessary to study this resource to turn it into a high value-added substance.

Porous carbon is usually prepared from biomass by adding different activators, such as zinc chloride and potassium hydroxide[9], for activation and transformation into multistage porous carbon. The preparation of multistage porous carbon by activation of biomass with potassium ferrate was in the news[10]. In fact, zinc chloride activation is one of the most widely used and effective methods to date[11,12].Given a porous carbon derived from Xanthoceras sorbifolium Bunge in the excellent properties of SCs and other fields, and also considering the richness of the reside of Xanthoceras sorbifolium Bunge oil after pressing (XSBOP).

Recently, Wang[13]discovered that expansion procedures of corn husk for capacitive corn husk carbon with a ahigh reversible capacity of 205.8 $mAhg^{-1}$.The reason is that the contribution of more solid electrolyte inter-phase via KOH activation.

Xiao [14]discovered that four-step procedures of coal for capacitive Coal-based porous carbon with a high reversible capacity of 421 F/g. Coal rank caused this result.

Wang[15]lotus-root like carbon matrix with porous struc-ture was fabricated via a two-step method. The reason is that the contribution of robust/porous, good conductivity .

Zhang[16]discovered that two-step expansion procedures of Xanthoceras sorbifoliaseed coats for capacitive Xanthoceras sorbifolia Bunge porous carbon with a specific capacitance of 421 F/g.

In this paper, a method of preparing multi-stage porous carbon from XSBOP and its application in the preparation of SCs are presented. The study will provide material for SCs, as well as a new way to recycle XSBOP. Our Xanthoceras sorbifolium bunge porous carbon hassuperior capacitive performance duo to the successful one-steps carbonized.

2. EXPERIMENTAL

2.1. Experimental method

Xanthoceras sorbifolium bunge used in this experiment was provided by Gansu Jingmao Ecological Agriculture Science and Technology Co., LTD. XSBOP and ZnCl2 were weighed and lapped evenly in a mortar. The mass ratios of XSBOP powder and ZnCl2 were 1:0, 2:1, 1:1 and 1:2. Then, the solid mixture was put into the tube futnace and heated to 800 ℃ in a high-temperature tubular furnace with nitrogen as a protective gas for carbonization. The heating rate was 5 ℃/min and the holding time was 2 h. Next, the product was soaked with 1 M/L HCl for 0.5 d, then washed with 3000 mL distilled water to neutral, and dried in a vacuum drying oven for 0.5 d to obtain the carbon material after pore expansion. The Xanthoceras sorbifolium Bunge multi-stage porous carbon was named as SPZ-X (1,2,3,4), according to mass ratios of 1:0, 2:1, 1:1, and 1:2.

2.2. Structural characterization

We use SEM ;BET;XPS and Raman to inspect and analyze the samples .

2.3. Electrochemical test

Using three electrodes in CHI660D electrochemical workstation, the electrochemical performance of KOH solution with a concentration of 6 M/L as electrolyte was determined. The samples were mixed with acetylene black and PTFE at the mass ratios of 16:3:1 to prepare material. The samples were uniformly coated on 2 cm^2 nickel sheets with area of 1 cm^2. The electrode was dried at 85 ℃ for 0.5 d in a drying oven, and then prepared at a pressure of 10 MPa. Impedance (EIS), cyclic voltammetry (CV) and Galvanostatic current charge-discharge (GCD) measurements were carried out on an electrochemical station using SCE as reference electrode and platinum foil as electrode.

$$\mathrm{C} = \frac{i\Delta t}{m\Delta V}$$

Where C is Specific capacitance (F/g), m (g) is the mass of the active material, Δt (s) is the discharge time, i (A) is the discharge current , and ΔV (V) is the voltage range [17,18]

3. RESULTS AND DISCUSSION

3.1. SEM and TEM

Fig.1a The carbon material prepared without pore expanding agent has almost no relatively smooth pores. With the addition of zinc chloride, a clear void structure can be seen. This structure is conducive to ion storage and migration of KOH electrolyte, thus showing excellent electrochemical performance (Fig.1b). By further magnification, regular distribution of micropores, mesopores and macropores could be seen at 500 nm (Fig.1c). It is analyzed that the Xanthoceras sorbifolium bunge porous carbon is graded and its electrochemical properties can be improved by improving its electric storage capacity. Transmission electron microscopy also verified that Xanthoceras sorbifolium bunge porous carbon SPZ-4 was composed of interconnected microporous structures (Fig.1d).

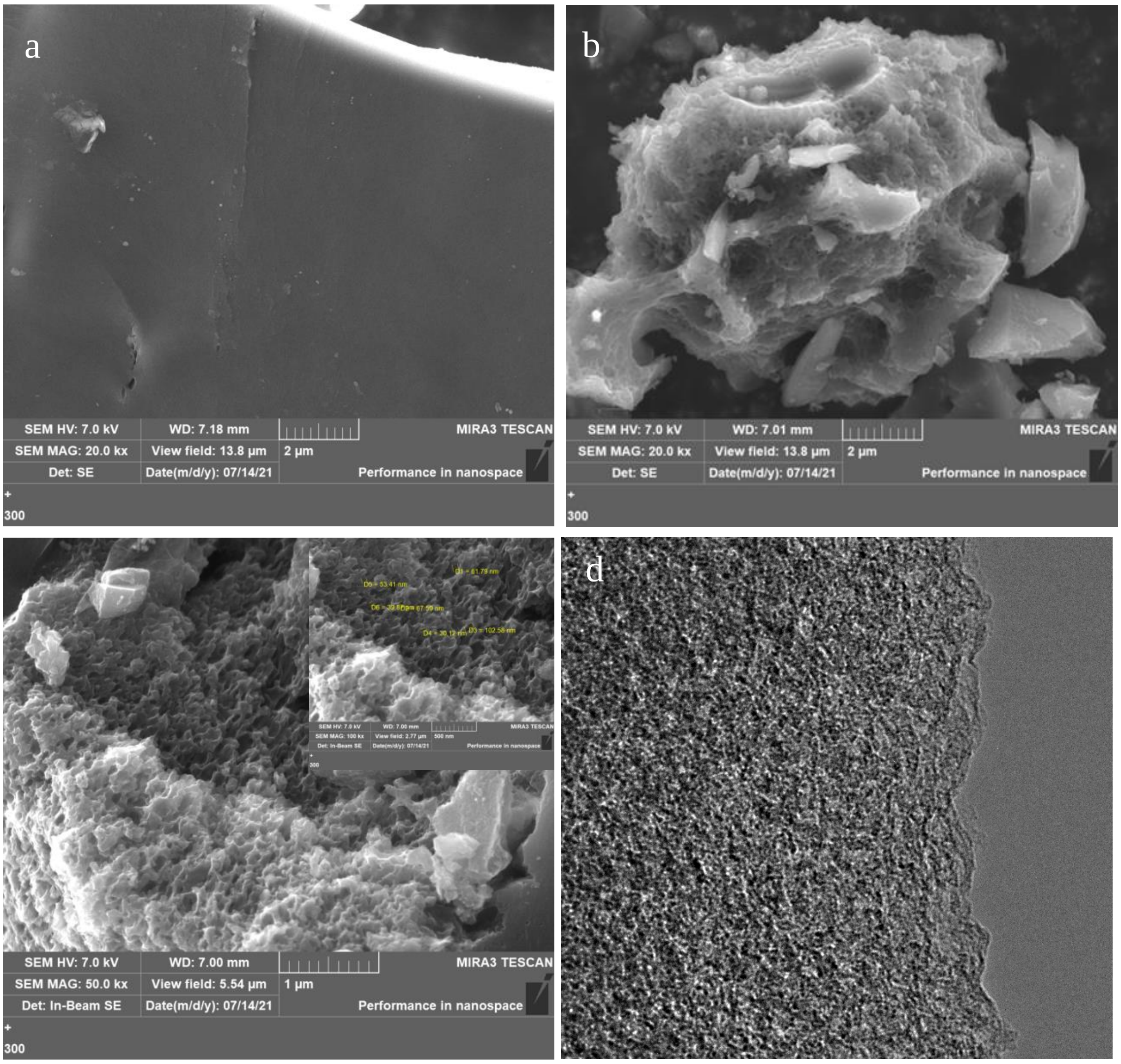

Figure 1. SEM image of (a) SPZ-1 (b,c) SPZ-4, TEM image of (d) SPZ-4

3.2. XRD and Raman analysis

Fig.2a is the XRD of Xanthoceras sorbifolium bunge porous carbon SPZ-1 and Xanthoceras sorbifolium bunge porous carbon SPZ-4. We can see that all samples have a near 24°, corresponding to (002) of graphitic carbon. We also can see that all samples have another peaks near 44°, corresponding to (100) of graphitic carbon, respectively. The crystal plane proves that the crystal of the Xanthoceras sorbifolium bunge porous carbon material has not changed.

We can see that there is a obvious characteristic peaks-D peak from Fig.2b, where D peak represents the disordered structure of the Xanthoceras sorbifolium bunge carbon material. We can see that there is a obvious characteristic G peak from Fig.2b, where G peak represents the graphitized structure of the Xanthoceras sorbifolium bunge carbon material[19,20]. The I_D/I_G values of SPZ-1 and SPZ-4 are 0.89 and 0.92, respectively. The results show that as the quality of $ZnCl_2$ increases, the degree of disorder increases. It is advantageous for the ions in the electrolyte to be rapidly transmitted by it crystal morphology.

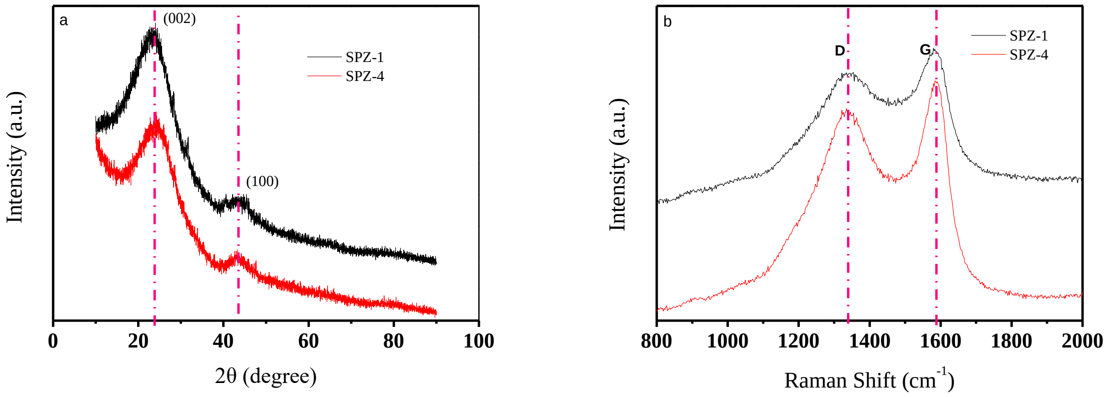

Figure 2. (a) XRD patterns of the samples, (b) Raman spectra of the samples

3.3. BET analysis

Xanthoceras sorbifolium bunge multi-stage porous carbon shows type IV adsorption/desorption isotherms according from IUPAC classification. The adsorption amount of nitrogen increased sharply at 0-0.3, indicating the existence of a large number of micropores in Xanthoceras sorbifolium bunge multi-stage porous carbon.

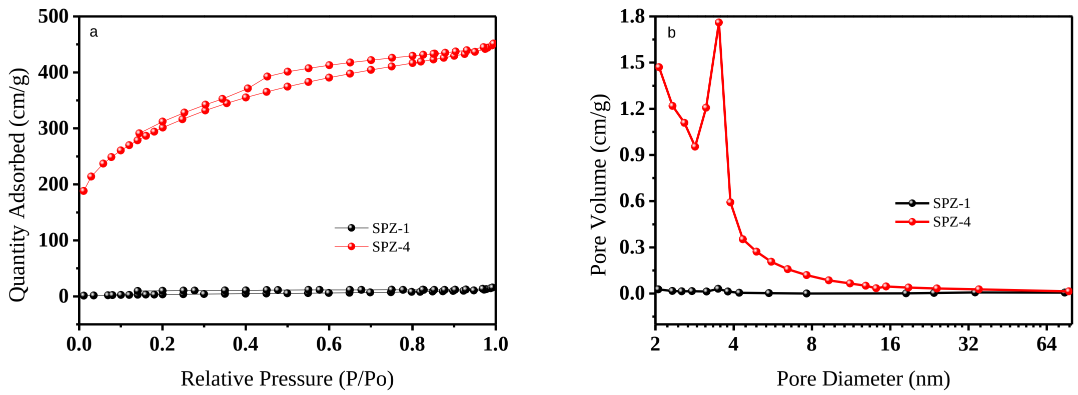

Figure 3. (a) N_2 adsorption/desorption isotherms and (b) the BJH pore size distribution curves of the Xanthoceras sorbifolium bunge multi-stage porous carbons.

Table 1. The pore size distribution of porous carbon

Sample	SBET① (cm2/g)	Vt② (cm3/g)	Dav③ (nm)	Vmic④ (cm3/g)	Vext⑤ (cm3/g)	Smic⑥ (cm2/g)	Sext⑦ (cm2/g)
SPZ-1	**14.8144**	**0.018**	**4.96**	**0.0136**	**0.0044**	**23.8538**	**21.7226**
SPZ-4	**1079.79**	**0.68**	**2.53**	**0.085**	**0.595**	**211.0606**	**868.7293**

①: BET surface area; ②: Total pore volume; ③: Average pore diameter; ④: Micropore volume; ⑤: External volume; ⑥: Micropore surface area; ⑦: External surface area

At higher relative pressures, obvious retention loops appear, indicating that there are a large number of mesopores, which is conducive to the production of more active sites and promotes the production of electrochemical reactions. Fig.3b is the pore size distribution image calculated by BJH method.

Table 1 lists the pore structures of Xanthoceras sorbifolium bunge porous carbon SPZ-1 and Xanthoceras sorbifolium bunge porous carbon SPZ-4. It can be seen from the picture that the specific surface area of the sample SPZ-4 is 1079.79 m^2/g and the total pore volume is 0.68 cm^3/g. The specific surface area of micropores is 0.595 m^2/g, which accounts for 87.5 % of the total specific surface area. The results show that there are more micropores in the structure of porous carbon.

3.5. XPS characterization

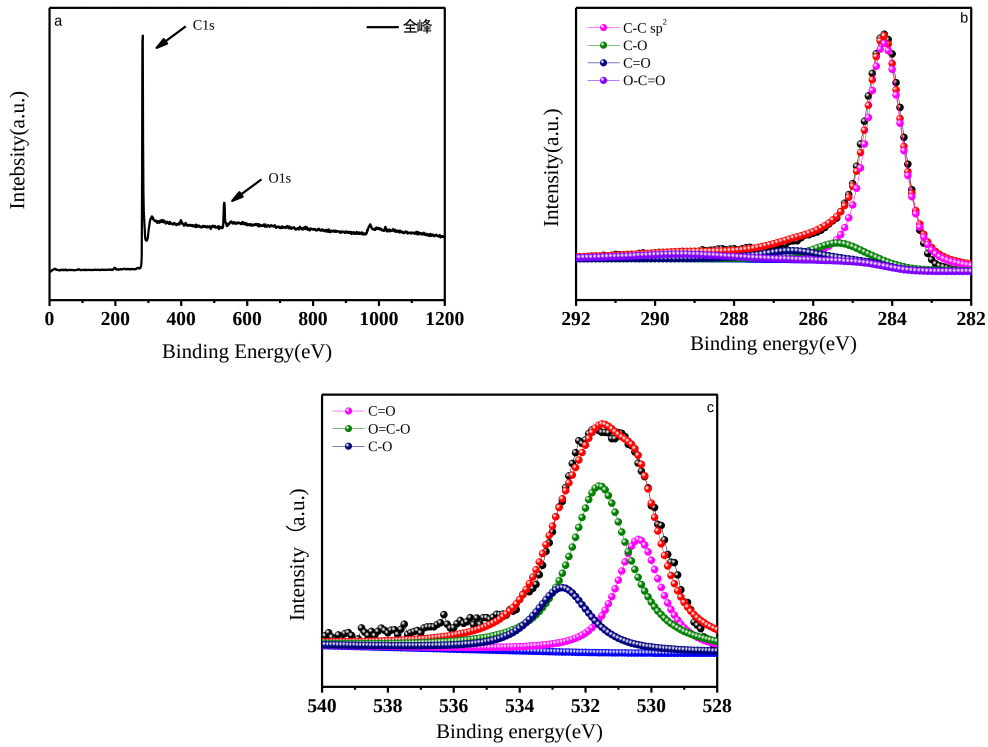

Figure 4. XPS full peak, C1s and O1s spectra of the SPZ-4 sample

The Xanthoceras sorbifolium bunge porous carbon SPZ-4 was characterized by XPS. There are C(95.18 wt%), N(0.14 wt%), and O(4.68 wt%) in the SPZ-4 sample. Fig.4a shows the full peaks of the SPZ-4.We can find only the C peak and the O peak. Fig.4c is the XPS spectrum of the C, we can see that there are C-O bond (285.5eV), C=C bond (284.6eV) , and C=O bond (286.5eV) [21]. The main C element is mainly C=C bond, and a small amount of C-O bond, C=O bond. Fig.4c is the XPS spectrum of the O, we can see that the O element of this material are mainly a C=O bond (532.7eV), C-O bond (531.6eV)[21], and O=C-O bond (533.7eV) [22].

3.6. Electrochemical analysis

At a current density of 1 A/g, the specific capacitances of Xanthoceras sorbifolium bunge porous carbon SPZ-1, SPZ-2, SPZ-3 and SPZ-4 are 11.2 F/g, 99.16 F/g, 197.3 F/g and 220 F/g. With the increase in $ZnCl_2$, the discharge time of the GCD image went up first but then it went down.

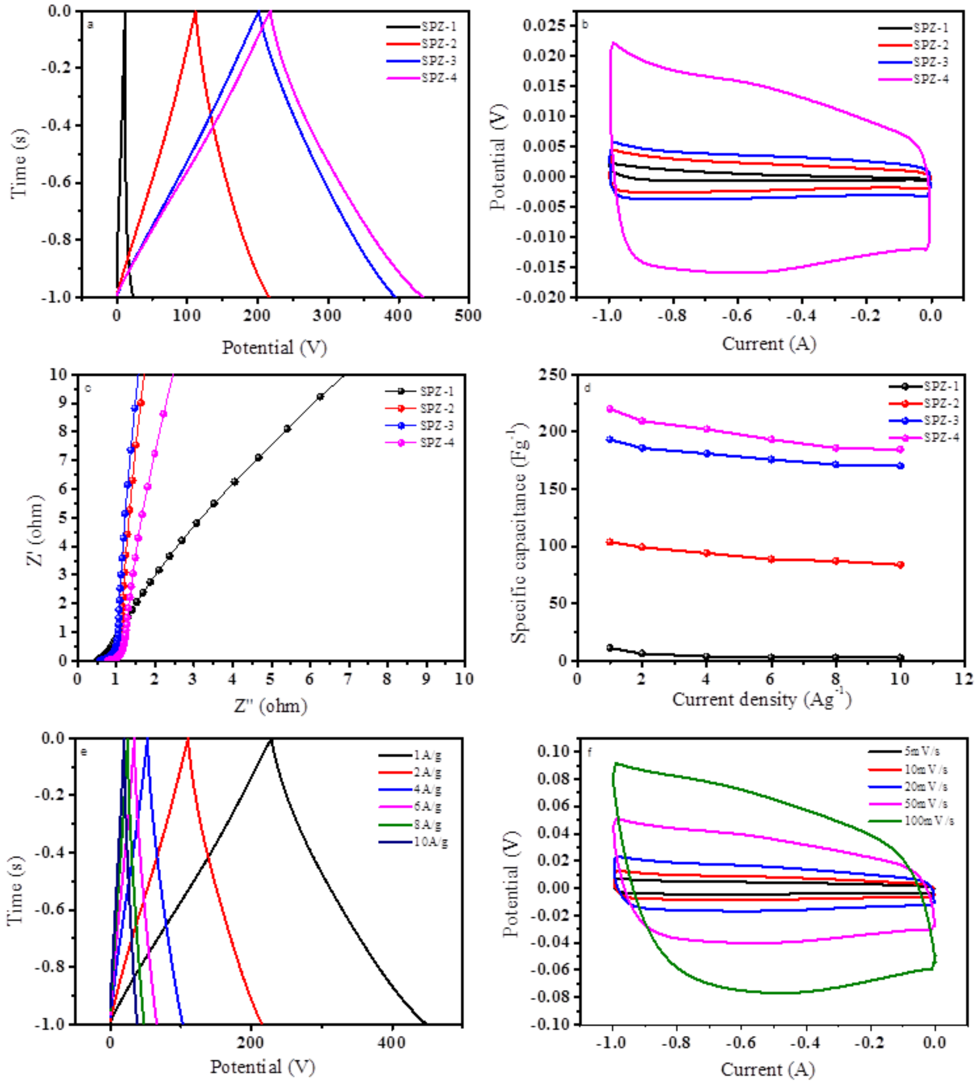

Figure 5. (a)Picture GCD;(b)picture CV;(c)picture EIS;(d) picture retention rate;(e) picture GCD at different current densities;(f) picture CV for wide range measurement.

Xanthoceras sorbifolium bunge porous carbon was made into electrode materials, and a three-electrode system was assembled with 6 M/L KOH solution to test the excellent performance of Xanthoceras sorbifolium bunge porous carbon. Fig. 5b is the CV curve of different activator ratios when the scan rate is 5 mV/s. We can see the CV image of the Xanthoceras sorbifolium bunge porous carbon SPZ-1 containing $ZnCl_2$ is good[23]. The results show that as the mass ratio of carbon source to $ZnCl_2$ increases, the closed area of the CV curve first increases and then decreases. Fig.5a is a constant current charge and discharge diagram of different activator ratios at a current density of 1 A/g. It can be seen from the figure that all samples are isosceles triangles. It can be seen from the figure that there is no voltage drop, which indicates that the prepared electrode material has good reversibility in the electrochemical test process. It can be seen from Fig.5d that the specific capacitance of the Xanthoceras sorbifolium bunge porous carbon SPZ-4 sample decreases to 79.6 % of the initial value.we can see that Xanthoceras sorbifolium bunge carbon SPZ-4 has the best electrochemical performance. we can see that that the activation of $ZnCl_2$ can promote the rate performance of the samples. In Fig.3c the results show that the Xanthoceras sorbifolium bunge porous carbon material has good transport and diffusion properties[24]. The Xanthoceras sorbifolium bunge porous carbon SPZ-4 is closer to the vertical axis, indicating that Xanthoceras sorbifolium bunge porous carbon SPZ-4 has the best transmission characteristics.We can see from the fig.5e that CV image are quasi-rectangular. The results show that Xanthoceras sorbifolium bunge porous carbon has good ion transport ability and maintains good rate performance. Fig.5f is the specific capacitance of Xanthoceras sorbifolium bunge porous carbon SPZ-4. We can see from the figure that the image of the Xanthoceras sorbifolium bunge porous carbon under different current densities are isosceles triangles.

Lists our results compared to previously published preparations of porous carbon

Table 2. Comparison of porous carbon with other materials

Materials	Specific capacitance(F/g) (current density)(A/g)	Electrolyte（KOH）	Referencces
Corncob	120 (0.5)	6 M	[25]
Camellia pollen	205 (0.5)	2 M	[26]
Rice husks	233 (2)	6 M	[27]
corn starch	162 (0.652)	6 M	[21]
Xanthoceras sorbifolium Bunge	220 (1)	6 M	This work

4. CONCLUSION

Porous carbon was the reside of Xanthoceras sorbifolium Bunge oil after pressing as carbon source and $ZnCl_2$ as the activator, the Xanthoceras sorbifolium Bunge porous carbon material was prepared. The morphology, microstructure and electrochemical properties of the Xanthoceras sorbifolium bunge porous carbon were studied. We prepared the Xanthoceras sorbifolium Bunge porous carbon SPZ-4 with the best electrochemical performance. The specific capacitance of Xanthoceras sorbifolium bunge porous carbon is 220 F/g in 1A/g. Xanthoceras sorbifolium bunge SPZ-4 porous carbon used as electrode material not only has excellent electrochemical performance and good charge transport ability, but also is a good carrier for preparing catalyst mesoporous materials.

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