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# Nitrogen-doped biomass-based hierarchical porous carbon with large mesoporous volume for application in energy storage



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## HIGHLIGHTS

- Hierarchical porous biochar is produced by nanowires PPy as poreforming substance.
- The product shows high specific capacitance (330 F g<sup>-1</sup>) and superior rate capability.
- The assembled coin-type symmetric supercapacitors shows high energy density.
- The product also possesses a high reversible capacity for lithium-ion battery.

#### ARTICLE INFO

Keywords: Crop waste N-doped biomass-derived carbon Hierarchical porous carbon Energy storage

# GRAPHICAL ABSTRACT



#### ABSTRACT

N-doped biomass-derived carbon with high specific surface area, suitable N atom doping ratio and superior hierarchical porous structure has been prepared by one-step carbonization activation method. Benefiting from the mesoporous structure formed by fragments of nanowires PPy anchoring to each other during the carbonization process, the product possesses large pore volume  $(1.53 \text{ cm}^3 \text{ g}^{-1})$  and mesoporous volume  $(1.01 \text{ cm}^3 \text{ g}^{-1})$ . Owing to the synergistic effect of the superior pore structure and suitable N atom doping ratio, the product exhibits excellent performance for energy storage. Typically, the product exhibits high specific capacitance  $(330 \text{ F g}^{-1})$  and rate capability (71.5% of capacitance retention at 20 A g<sup>-1</sup>) in three-electrode systems. A cointype symmetric supercapacitor has been assembled based on the product, and an energy density as high as 37.5 W h kg<sup>-1</sup> is verified in this cell. Furthermore, the product is also applied to the area of lithium-ion battery, where a high reversible capacity of 1662 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup> is confirmed, indicating the superior Li<sup>+</sup> storage capability.

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## 1. Introduction

In recent years, with the rapid consumption of limited fossil resources, there has been an urgent need for developing sustainable, efficient and green energy storage devices (ESDs, such as lithium-ion battery and supercapacitors) [1]. As we all know, carbon materials are commonly used as an electrode material in ESDs due to their chemical stability, high surface area and adjustable surface functional groups [2]. Many carbon materials, such as carbon nanotubes [3], graphene [4] and activated carbon [5] have been intensively investigated for ESD electrodes. Among them, biomass-derived activated carbon, owing to their significant advantage of low cost and well-developed pore structure, has been considered as the first candidate for commercial ESDs [6].

Many researchers have made efforts to develop the biomass-derived carbon applied to ESDs [7], and achieved some excellent products. For example, Chen et al. reported the elm samara derived highly porous carbon nanosheets with outstanding capacitive performance [8]; Niu et al. synthesized high defect density active carbon (based on cattle bone) with good lithium ion storage capacity [9]; Cheng et al. prepared squid ink-based hierarchically porous carbon with excellent capacitive performance [10]. Obviously, all of the above excellent carbon materials are derived from some special biomass (they either possess special biomass structure or special composition, as shown in Table SI 1). However, this is not advisable based on cost consideration due to the rareness of these biomass raw materials.

Crop wastes are an abundantly and readily available biomass, but their harmless treatment has brought tremendous pressure on the environment and finance for governments all over the world. The crop waste is rich in cellulose [11], which is an excellent carbon source for ESD application. Therefore, some researchers are devoted to the development of crop waste derived carbon [12,13]. Unfortunately, the results are unsatisfactory due to the fact that the singe microporous structures result in low specific surface area utilization for this kind of material (even though it has the high specific surface area). It is because of the naturally hydrophobic carbon matrix surface. It means that the accessible specific surface area is greatly limited by the highly-developed microporous, although these microporous structures can lead to a high specific surface area [14]. Therefore, enhancement of the wettability is an effective way to increase the accessible specific surface area and thus the electrochemical performance for this kind of material.

In the past few years, doping heteroatoms into carbon matrix has been proved a valid method for improving the wettability and conductivity of carbon materials [15]. Particularly, doped N heteroatoms has an different electronegativity with C atoms, which will provide not only improved wettability, but also more polarized surface and a fast transfer rate of electrolytic ion of the carbon matrix [16]. The traditional synthetic pathway of N-doped biomass derived carbon is posttreatment precursor carbon with reaction nitrogen sources (such as nitric acid, urea and ammonia) [17,18]. This approach has improved the electrochemical performance of biomass-derived carbon to some extent. However, it is worth noting that the fundamental problem of crop waste derived carbon mentioned above (single microporous structure) has not been solved by this approach.

In this study, a common crop waste, sugarcane bagasse (SB), was used as a carbon source for ESDs. SB-derived carbon (SBC) exhibits interconnected framework, very benefit for ion diffusion [19,20]. We also doped nanowires of polypyrrole (PPy) into the SBC matrix to further improve its performance. It is based on the following considerations: i) A key strategy to improve the specific surface area utilization of carbon materials is to build hierarchical porous structure combing micro-, meso- and macropores [8]. ii) Some recent studies have shown that polypyrrole (PPy) is an effective N source for N-doped carbon due to the fact that the derived carbon is rich in pyrrolic N (a good electrondonor) [21–23]. We expect that the nanowire structure of PPy can combine with interconnected framework of SBC to construct hierarchical porous structure for overcoming the fundamental problem of SBC. Our morphological and electrochemical evaluations in the current study corresponds to our design: The target product possesses the hierarchical porous structure following our synthesis strategy and exhibits superior electrochemical performance (high specific capacity, excellent rate capacity and outstanding cycle stability) in the applications for both supercapacitors and lithium-ion batteries. This synthesis strategy may bring hope for other common crop waste derived carbon applied to ESDs.

## 2. Experimental

### 2.1. Sample preparation

The original SB used was collected from Guangxi province, China and cut into small pieces. SB pieces (4.0 g) were refluxed in 100 mL deionized water at 90 °C for 4 h to remove the dirt. SBC was prepared by KOH activation method using the mixture of cleaning SB pieces and KOH as the precursor. The mass ratio of SB pieces and KOH was 1:1. The mixture was stirred in 20 mL ethanol for 2 h, dried at 60 °C to evaporate the ethanol, and pyrolyzed at 800 °C (5 °C min<sup>-1</sup>) for 2 h under Ar atmosphere. Afterwards, the obtained sample was washed by 1 M HCl, followed by water for several times (until filtrate is added to the 0.1 M AgNO<sub>3</sub> solution without precipitation). Finally, the sample was dried at 80 °C for 12 h before the next step.

The SBC/PPy composite was prepared by in-situ polymerization reaction. Typically, SBC (100 mg) and hexadecyl trimethyl ammonium bromide (CTAB, 303 mg) were added to 30 mL 1 M HCl and then dispersed with sonication for 20 min. 100  $\mu$ L pyrrole was added into the above mixture and vigorously stirred for 2 h. Afterwards, 10 mL ammonium persulfate (APS) aqueous solution (0.33 M) was added drop by drop to the mixture with vigorous stirring. The reaction was carried out at room temperature for 2 h, and the final product was washed and dried at 80 °C for 12 h to obtain the SBC/PPy composite.

NPSBC was synthesized by one-step carbonization activation method. SBC/PPy composite and KOH was mixed at a mass ration of 1:1 and fully milled in a mortar. The mixture was placed in a tubular furnace and calcined at 800 °C (with heating rate of  $5 \,^{\circ}$ C min<sup>-1</sup>) for 2 h under Ar atmosphere, followed by washing with HCl solution and water for several times (the washing process is the same as that of SBC), and dried at 80 °C for 12 h. For comparison, N-doped porous nanowires PPy derived carbon (NPPC) was prepared by the same process. In addition, SBC/PPy composite derived carbon (NSBC) was also prepared by the above process except that KOH was not added.

#### 2.2. Material characterization

Scanning electron microscopy (SEM, HITACHI S-4800), transmission electron microscopy (TEM, TECNAI F30), X-ray diffraction (XRD, Rigaku mini Flex 600 with Cu Ka radiation) and Raman spectroscopy (HORIBA Xplora) were employed to investigate the morphology, the microstructure, the crystallographic structure and the defect of samples. X-ray photoelectron spectroscopy (XPS) was performed on PHI Quantum 5000 equipped with an Al Ka radiation source. Specific surface area and pore size distribution were analyzed via nitrogen adsorption-desorption method at liquid nitrogen temperature  $(-196 \degree C)$ on a Micromeritics ASAP-2020 analyzer. The surface chemical function groups were confirmed by Fourier transform infrared spectroscopy (FTIR, Nicolet IS5 spectrometer). The elemental analysis was performed by Elemental Analyzer (Vario EL III, Elementar Analysensysteme GmbH, Germany). The trace metal element content of SB and SBC was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, NCS Testing Technology Co., Ltd.). The 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte wettability to SBC, NPPC and NPSBC was confirmed by contact angle measurement (a commercial drop shape analysis system is employed, Powereach JC2000C1, Shanghai Zhougchen



Scheme 1. Schematic illustrations of the preparation process of NPSBC.

Digital Technique Equipment Co. Ltd., China). The test electrode was prepared by loading sample slurry (contains 90 wt% sample, 5 wt% acetylene blank and 5 wt% polytetrafluoroethylene) on a copper foil, and then dried at 80 °C for 12 h. The conductivity of samples was measured by four probes method (four-probe resistance/square resistance tester, Kund Technology, Guangzhou, China). For the conductivity test, all samples were prepared in pellet form (the diameter and thickness of pellet were 13 and 0.6 mm, respectively) at a pressure of 50 MPa.

#### 2.3. Electrochemical measurements

For supercapacitors (SC) test, all the electrochemical performances were measured on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) at room temperature in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The active material slurries prepared by mixing the samples (90 wt%), acetylene blank (5 wt%) and polytetrafluoroethylene (PTFE, 5 wt%) were coated onto a stainless mesh  $(1 \times 1 \text{ cm}^2)$  and then dried at 80 °C for 12 h. Finally, the stainless mesh was compressed at 10 MPa for 5 min (the mass loading of active materials was about 3 mg). A three-electrode system was used to investigate the individual electrode with platinum foil as the counter electrode and saturated calomel electrode as the reference electrode. The electrochemical performance of the whole NPSBC-based symmetric supercapacitors was determined in a two-electrode cell configuration (CR2032 coin-type cell). The two electrodes preparation was still carried out as described above method (current collector was stainless mesh with a diameter of 12 mm, mass loading of active materials was about 1 mg), and they were separated by filter paper. The cyclic voltammetry (CV), galvanostatic charge/ discharge (GCD) and electrochemical impedance spectroscopy (EIS, frequency range from 0.01 to 100 000 Hz, were carried out at open circuit potential with as ac perturbation of 5 mV) tests were performed in three-electrode systems and the whole symmetric supercapacitors, respectively.

The specific capacitance of single electrode in the three-electrode

system was calculated from the GCD curves by the Eq. (1) [24]:

$$C_{sp} = \frac{I \times t}{\Delta V \times m} \tag{1}$$

where I, t,  $\triangle V$  and m are discharge current, discharge time, potential window and mass of active material, respectively.

The specific capacitance of the whole symmetric supercapacitors was obtained by the Eq. (2) [25]:

$$C_{cell} = \frac{I \times t}{\Delta V \times M} \tag{2}$$

where M is the total mass of the positive and negative electrodes. The energy density (E,  $W h kg^{-1}$ ) and power density ( $W kg^{-1}$ ) of symmetric supercapacitors were calculated via the Eqs. (3) and (4) [25]:

$$\mathbf{E} = \frac{1}{2} C_{cell} (\Delta V)^2 \tag{3}$$

$$p = \frac{E}{t}$$
(4)

The electrochemical performance of the lithium-ion battery (LIB) was carried out using 2016 coin-type cell with the lithium metal as counter electrode, and the working electrode preparation method was similar to SC test except that the collector was replaced by nickel foam (diameter of 12 mm, the mass loading of active materials is about 2.8 mg). Moreover, Celgard 2400 and 1 M LiPF<sub>6</sub> solution with a mixture of ethylene carbonate and diethyl carbonate (1:1 v/v) as separator and electrolyte, respectively. The whole assembly process under an Ar atmosphere in a dry glovebox. The GCD tests were carried out a battery testing system (Land CT2001A) within a voltage range of 0.01–3 V at different current densities. CV data were still collected by using CHI 660D electrochemical workstation at the scan rate of 0.1 mV s<sup>-1</sup>.



Fig. 1. SEM images of SBC/PPy (a, b), NPSBC (c, d); TEM images of NPSBC (e, f); dark-field TEM, C, O and N elemental mapping STEM images of NPSBC (g).

## 3. Results and discussion

#### 3.1. Morphological and structural characterization

The preparation process of target sample is shown in Scheme 1. SBC was prepared via KOH activation method; the surface of SBC was coated by nanowires PPy (SBC/PPy composite) by in-situ polymerization reaction; finally, an interesting phenomenon was discovered, the nanowires PPy on the surface of SBC charged into the fragment carbon, and these fragments anchored each other to form the mesoporous structure after the one-step KOH carbonization activation process (was confirmed by SEM and TEM images). Till now, the target sample NPSBC was prepared. SEM and TEM were used to examine the morphology of samples and the results were shown in Fig. 1 and SI 1. Obviously, SBC exhibits macroporous structure and highly interconnected frameworks, and the sizes of macropores are in the range of  $1-5 \,\mu\text{m}$  (as shown in SI 1), which are beneficial to the mass transport and ions approach adsorption sites. The interconnected frameworks of SBC were coated by nanowires PPy (is clearly observed in Fig. 1a and b) in SBC/PPy. The FTIR and XRD spectra of SBC/PPy confirm the characteristic peaks of PPy (as shown in SI 2, for FTIR, the peak at  $1622 \text{ cm}^{-1}$  is for C=N [26], and for XRD, only a broad peak appeared at 21.5°, which is assigned to the amorphous structure of PPy [27]). All of these results indicate that the SBC/PPy composite was successfully prepared. The target sample NPSBC is obtained by one-step carbonization activation of SBC/PPy and its excellent microstructure is also implied by SEM (as shown in Fig. 1c and d). It is noteworthy that, different from conventional point of view, the nanowire structure of PPy on the surface of SBC has not been maintained, but has transformed into fragments carbon anchoring to each other to form the mesoporous structure. The peculiar mesoporous structure of NPSBC is further demonstrated by TEM images (Fig. 1e and f). The elemental mappings of C, O and N in NPSBC are revealed in Fig. 1g. The existence and uniform distribution of N is verified, suggesting that the N atoms are successfully incorporated onto the surface of SBC.

To investigate the graphitization degree (GD) of samples, Raman spectroscopy was employed. As shown in Fig. 2a, all Raman spectra can be fitted into four peaks centered at 1242, 1349, 1510 and 1595 cm<sup>-1</sup>, which can be assigned to the I, D, D" and G bands, respectively. The D band, is attributed to the disorder induced by defect sites on the graphitic plane; the G band, is generally observed in all biomass derived carbon and attributed to the stretching bond of sp<sup>2</sup> hybridized carbon; the I band, is derived from impurities or heteroatoms (for NPPC and NPSBC, it is derived from the heteroatoms of N and O; for SBC, it is only derived from the heteroatoms of O) on the graphitic plane; the D" band, is assigned to the defects in graphene layer stacking [9,28]. The GD of samples can be represented by the area ratio of D and G bands (I<sub>G</sub>/I<sub>D</sub>),

and obviously, the NPSBC exhibits increased GD than the other samples, mainly due to the increase of GD of SBC when SBC undergoes secondary carbonization. Moreover, the GD of NPPC is higher than that of SBC, indicating that the GD of polymer derived carbon is higher than that of biomass derived carbon, and this is another reason for the increase of GD of NPSBC. Similar results are obtained from XRD spectra, i.e., two broad peaks derived from the (002) and (101) diffraction of graphitic carbon can be observed at around 25° and 43° in all samples, respectively (as shown in SI 3), and the enhanced diffraction intensity of NPSBC still reveals its high GD [29]. In addition, the I band content of NPSBC is significantly larger than that of the other samples, because the NPSBC possesses the most heteroatoms (confirmed by XPS spectra). At the same time, the D" band contents of NPSBC and NPPC are much larger than that of SBC, indicating NPSBC and NPPC possess a large number of graphene layer stacked structures, and these structures will further improve their conductivity.

To directly reveal the excellent hierarchical porous structure of the NPSBC, the nitrogen adsorption-desorption tests were performed, and the results are shown in Fig. 2b and summarized in Table 1. The same as the common biomass derived carbon, the isotherm plot of SBC mainly displays typical type-I isotherm, indicating a large number of micropores. Moreover, a small number of mesopores are also found by the slight hysteresis loop in the range of 0.45-1 P/P<sub>0</sub> [30]. For NPPC, its isotherm plot shows a similar shape to SBC, except for the more pronounced hysteresis loop, which suggests more contribution of mesoporous to the total pore volume (as shown in Table 1, the value of  $V_{mes}$ / Vt is 0.44). Compared with SBC and NPPC, NPSBC can be observed that the most obvious hysteresis loop in its isotherm plot, suggesting the bigger contribution of mesoporous structure to total pore volume than that of SBC and NPPC. This phenomenon is attributed to the fact that, in the process of one-step carbonization activation, the macromolecular chain of PPy undergoes the randomly rupture, while for the SBC/PPy composite, the fragments of break are easier to anchor to each other to form the mesoporous structure than that of pure PPy by the limiting effect of the SBC to PPy molecules (is revealed by SI 4b, the distribution of pure PPy derived fragments is more scattered than that of SBC/PPy derived fragments). The isotherm plot of NSBC is shown in SI 7, and the specific surface area of NSBC  $(518 \text{ m}^2 \text{ g}^{-1})$  is far less than that of NPSBC. Furthermore, different from NPSBC, the hysteresis loop of NSBC appears in high pressure, indicating the existence of macroporous structure by particles stack, and the mesoporous structure formed by fragments of nanowires PPy disappeared. This phenomenon reveals that KOH presence is a key factor for formation of mesoporous structure in the one-step carbonization activation process. Overall, the excellent hierarchical porous structure of NPSBC is constructed via SBC as the framework and nanowires PPy as the mesoporous forming substance, and the special structure will effectively improve the utilization of



Fig. 2. Raman spectra (a), nitrogen adsorption/desorption isotherm and pore size distribution (b) of NPSBC, NPPC and SBC.

specific surface area.

The chemical contents and valence states of each element in samples were examined by XPS spectra. Obviously, a strong C 1s peak and a dominant O 1s peak are observed in XPS full spectra of all samples (SI 5a), indicating the KOH activation method can make a lot of O element doped into carbon framework. In addition, a weak N 1s peak is observed in NPSBC and NPPC samples (SI 5a), suggesting that N-doped carbon materials have been successfully prepared. The content of C, N and O in samples were further measured by elemental analysis and the results are summarized in Table 1. It is clear that the N content of NPSBC is higher than that of NPPC, which suggests that the interaction of SBC and PPy has a certain protective effect on reserved N element when PPy experiences KOH one-step carbonization activation. Besides the chemical content, the carbonization activation process also affects the chemical bonds of each element. The high resolution XPS spectra of each element were further fitted by the Gaussian-Lorentzian curve-fitting method (as shown in Fig. 3) [31]. The C 1s peak of NPSBC and NPPC, can be fitted into four peaks centered at 284.1, 285.2, 286.2 and 288.4 eV, attributed to C-C/C-H, C-O, C-N/C=N and C=O bond [32], respectively. Similarly, the C1s peak of SBC can be fitted by three peaks (C-C/C-H, C-O and C=O, SI 5b), and the content of C-C/C-H is less than that of NPSBC and NPPC, which is consistent with the Raman spectra analysis results. The N 1s peak of NPSBC and NPPC can be fitted into three peaks ascribed to the pyridinic N (at 398.7 eV, N-1), pyrrolic N (400.2 eV, N-2) and graphitic N (401. 7 eV, N-3), respectively

[33]. For N-1, it is combined with two carbon atoms and donates a p electron to the aromatic  $\pi$ -conjugated rings, and thus it has higher charge mobility and further improves electrochemical performance. N-2 has a huge contribution to the pseudocapacitance due to its good electron-donor characteristics [34,35]. Apparently, the N-1 and N-2 contents of NPSBC are much higher than that of N-3, which predicts the excellent electrochemical performance of NPSBC. In addition, N-1 and N-2 can also significantly improve the interface of electrode/electrolyte (confirmed by SI 6, the contact angle of NPSBC and NPPC are less than that of SBC) by reinforce the carbon surface activity. More importantly, the contact angle of NPSBC is greater than that of NPPC (as shown in SI 6), which reveals that the N content of NPSBC is mainly distributed the external surface. Furthermore, it should be noted that the obvious O content would have a positive impact on the wettability of samples, and further improve the utilization of specific surface area. From O 1s peaks of Fig. 3, the peak at 530.8 eV attributed to C-OH/C=O, the peak at 532.4 eV ascribed to C-O-C, and the peak at 534.2 eV assigned to C-O=C [36], suggesting that there are abundant O-containing functional groups on the surface of samples.

In brief, the target product NPSBC was successfully prepared by onestep carbonization activation method using SBC as the carbon framework and nanowires PPy as pore-forming substance. It possesses the excellent hierarchical porous structure, high specific surface area and suitable heteroatom doping ratio. Thus, it is predicted to have outstanding electrochemical performance when it applies to ESDs.

Table 1	L
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Pore structure	narameters	and	compositions	of NPSCB	NPPC and	SBC
Fore structure	parameters	anu	compositions	or mesco,	NFFG anu	SDC.

Sample ID	Pore structure parameters						Elemental analysis			
	$S_{BET}/m^2 g^{-1}$	D <sub>av</sub> (nm)	$V_{T}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{mic} (cm^3 g^{-1})$	$V_{mes} (cm^3 g^{-1})$	$V_{mes}/V_T$	C/wt%	O/wt%	N/wt%	H/wt%
NPSBC	2232	3.82	1.53	0.51	1.01	0.66	83.3	12.1	3.1	1.3
NPPC SBC	1690 1540	3.21 3.09	1.08 0.88	0.56 0.63	0.48 0.21	0.44 0.24	86.5 90.1	10.2 8.3	2.0 0.1	1.1 1.2

Dav: average pore diameter; V<sub>T</sub>: total pore volume; V<sub>mic</sub>: micropores volume; V<sub>mes</sub>: mesoporous volume.



Fig. 3. High resolution C 1s, O 1s and N 1s XPS spectra of NPSBC and NPPC.

## 3.2. Electrochemical performances of samples for supercapacitors

The capacitive performance of samples were investigated in a threeelectrode system by CV, GCD and EIS measurements, and the results are shown in Fig. 4. Apparently, the CV curves of all samples (Fig. 4a, at a scan rate of  $0.01 \text{ V s}^{-1}$ ) exhibit a well symmetric rectangular shape and NPSBC shows the maximum current response, indicating their dominant behavior of ideal electrochemical double-layer capacitance (EDLC) and the large specific capacitance of NPSBC [37], respectively. Furthermore, a pair of weakly broadened humps are observed on the CV curves of NPSBC and NPPC, attributing to the limited pseudocapacitance from the doped N atoms [38]. Correspondingly, the GCD curves of all samples (Fig. 4b, at a current density of  $1 \text{ A g}^{-1}$ ) show a nearly triangular symmetry also due to their dominant ideal EDLC behavior. The specific capacitance of samples is calculated from the discharge curves and summarized in Table 2. NPSBC achieves the largest specific capacitance (330 F g<sup>-1</sup>), and it is about 2 times and 1.3 times higher than that of SBC (160 F g<sup>-1</sup>) and NPPC (252 F g<sup>-1</sup>), respectively. The increased capacity may be owing to two aspects: i) the improved specific surface area and its utilization from mesoporous structure, and ii)



Fig. 4. CV (a, scan rate of  $0.01 \text{ V s}^{-1}$ ), GCD (b, current density of  $1 \text{ A g}^{-1}$ ) of SBC, NPPC and NPSBC; specific capacitance versus current density of NPSBC (c); EIS curves (d) of SBC, NPPC and NPSBC.

#### Table 2

Comparison of the specific capacitance for previously reported porous carbon materials.

Carbon type	Electrolyte	Current density (A $g^{-1}$ )	Mass loading (mg cm $^{-2}$ )	Potential range (V)	Specific capacitance ( $\mathrm{F}\mathrm{g}^{-1})$	Refs.
Bamboo derived carbon	6 М КОН	0.5	~1.5	-1.0 ~ 0	222	[2]
Willow catkin derived carbon	6 M KOH	0.5	~4.4	$-1.0 \sim 0$	298	[18]
Rice straw derived carbon	6 M KOH	0.5	3.0 ~ 6.0	$-1.0 \sim 0$	337	[12]
Pomelo peel derived carbon	6 M KOH	1.0	~2.0	$-1.0 \sim 0$	278	[39]
Silk derived carbon	$1 \text{ M H}_2\text{SO}_4$	0.1	~ 3.2	0 ~ 1.0	264	[40]
Lotus pollen derived carbon	EMIMBF <sub>4</sub>	1.0	~9.2	0 ~ 3.5	207	[41]
Seaweeds derived carbon	$1 \text{ M H}_2\text{SO}_4$	0.2	_	$-1.3 \sim 0.6$	264	[42]
Enteromorpha prolifera derived carbon	6 M KOH	1.0	_	0 ~ 1.0	260.6	[43]
PPy derived mesoporous carbon	6 M KOH	1.0	_	$-1.0 \sim 0$	180	[22]
KOH activation of graphene oxide	6 M KOH	1.0	~0.7	0 ~ 0.8	188	[44]
N-doped graphene aerogels	6 M KOH	0.2	2.2 ~ 3.0	$-1.0 \sim 0$	197	[45]
Graphene hydrogel films	6 M KOH	1.0	_	0 ~ 0.8	183	[46]
NPSBC	$1 \ \mathrm{M} \ \mathrm{H_2SO_4}$	1.0	1.0 ~ 3.0	$-0.4 \sim 0.6$	330	This work

the improved surface wettability and pseudocapacitance from doped heteroatoms. The specific capacitance of NPSBC is higher than or close to many of the biomass-derived carbons reported in the literature, even better than some mesoporous carbon and graphene-based materials (as shown in Table 2).

The effect of the current densities on the specific capacitance of samples was studied (performed by GCD measurement) to reveal the outstanding rate capability of NPSBC, and the results are shown in Fig. 4c. Basically, the specific capacitance of samples decreases gradually with the increase of current density, and this is due to the electrolyte ions do not have enough time to diffuse into the entire pores [47]. However, NPSBC still retains 236 F g<sup>-1</sup> at 20 A g<sup>-1</sup>, and the capacitance retention is 71.5% (compared with 330 F g<sup>-1</sup>, at  $1 \text{ A g}^{-1}$ ). For NPPC and SBC (specific capacitances are 145 F g<sup>-1</sup> and 81 F g<sup>-1</sup> at  $20 \text{ Ag}^{-1}$ , respectively), their capacitance retentions are 57.5% and 50.6%, respectively, far less than NPSBC. Moreover, it is clear that the capacitances of NPPC and SBC are more significantly reduced than that of NPSBC at 10–20 A  $g^{-1}$ . All of the above indicate that NPSBC possesses the outstanding rate capability especially at high current densities, and all these results are mainly derived from the external surface N-doped mesoporous structure act as the reservoirs for electrolyte ion (which can promote the rapid transfer of ion). The EIS spectra were further employed to reveal the charge transport and ion diffusion process, and the Nyquist plots of the samples are showed in Fig. 4d. In addition to SBC, NPSBC and NPPC present similar shapes, containing a small semi-circle at high frequency, which corresponds charge transfer resistance (Rct); a nearly diagonal line corresponding to Warburg impedance (R<sub>w</sub>) at medium frequency, representing the diffusion rate of ion into the microporous surface of samples; a steep linear line at low frequency, corresponding to ideal capacitive performance [48,49]. Obviously, NPSBC has low  $R_{\rm ct}$  and  $R_{\rm w}$  due to the fact that it shows a small diameter of semi-circular and a short diagonal line at high and medium frequency, respectively. For SBC, the EIS plots do not exhibit semi-circle, and this is may be due to its low faradaic resistance [50]. Moreover, the intercept at the Z' axis reveals the internal resistance  $(R_i, R_i)$ including electrolyte resistance, material resistance and contact resistance between material and current collector) [51]. The R<sub>i</sub> of NPSBC, NPPC and SBC is about 0.76, 0.97 and 1.12  $\Omega$ , respectively, and these results are consistent with conductivity test (as shown in Table SI 2, the conductivity of SBC, NPPC and NPSBC are 0.04, 0.84 and 0.45 S cm<sup>-1</sup>, respectively), suggesting that N doping can effectively improve the conductivity of carbon materials. In sum, EIS measurements further reveal that NPSBC exhibits the low R<sub>ct</sub>, R<sub>w</sub> and R<sub>i</sub> owing to its suitable heteroatom doping ratio and ions accessible hierarchical porous structure, and the results are consistent with analysis of CV and GCD. The cycle stability of NPSBC has also been investigated by GCD measurement at a current density of  $10 \,\text{Ag}^{-1}$  for 5000 cycles, and the results are shown in SI 8b. The specific capacitance of NPSBC is reduced slightly and the capacitance retention is 96.6% after 5000 cycles,

meaning superior cycle stability. More importantly, the broadened humps of CV curve largely disappear after 5000 cycles (the inset of SI 8), revealing that the capacitance reduction is mainly due to the recession of heteroatoms pseudocapacitance.

To further reveal the outstanding capacitive performance of NPSBC, a coin-type symmetric supercapacitors is assembled (positive and negative electrode materials are both NPSBC, denoted as NPSBC// NPSBC), and its performance test results are shown in Fig. 5. The potential window is an important factor for real supercapacitors, which directly affects the power and energy density of supercapacitors. CV measurements were first executed in order to determine the potential window of NPSBC//NPSBC, and shown in Fig. 5a. Basically, the current response of NPSBC//NPSBC increases as the potential window increases, especially in the range of 0-0.75 V. This is attributed to the doped heteroatoms which has undergone the reversible redox reactions, indicating that the EDLC and slight pseudocapacitance are simultaneously exist. Besides, there is no significant increase of anodic current even at 1.5 V, yet, the anodic current dramatically increased at 1.6 V (as shown in SI 10a), which indicates that the electrolyte has been decomposed into hydrogen and/or oxygen [52]. Thus, the suitable potential window of NPSBC//NPSBC is  $0 \sim 1.5$  V. The GCD test were performed at various current densities in 0-1.5 V and the results are shown in Fig. 5b. Corresponding to CV measurements, the GCD curves of NPSBC//NPSBC (the inset of Fig. 5b) have a slight deviation from the triangular symmetry at 0-0.75 V, and this still reveals the presence of pseudocapacitance. The specific capacitance of NPSBC//NPSBC is decreased with increasing current density, but has a slight drop at the current density of 10–20 A g<sup>-1</sup>. Furthermore, the capacitance retention is 66.7% at 20 A  $g^{-1}$  (the specific capacitance is 120 and 80 F  $g^{-1}$  at 1 and  $20 \text{ Ag}^{-1}$ , respectively). These results suggest that NPSBC still possesses the excellent rate capability in real supercapacitors.

The Ragone plots of NPSBC//NPSBC based on the mass of active substance are shown in Fig. 5c. A high energy density of  $37.5 \text{ W h kg}^{-1}$ is reached with the power density of 750  $W\,kg^{-1},$  and 22.2  $W\,h\,kg^{-1}$ could be delivered at  $23505 \text{ W kg}^{-1}$ . The values are superior to previously reported biomass derived carbon-based symmetric supercapacitors, such as pomelo peel derived carbon  $(9.4 \text{ W h kg}^{-1} \text{ at})$  $100 \text{ W kg}^{-1}$ ,  $17.1 \text{ W h kg}^{-1}$  at  $3854 \text{ W kg}^{-1}$  and  $20 \text{ W h kg}^{-1}$  at  $400 \text{ W kg}^{-1}$  [39,53,54], batatas stalks and leaves derived carbon  $(25.8 \text{ Wh kg}^{-1} \text{ at } 250 \text{ Wkg}^{-1})$  [48], poplar catkins derived carbon  $(19.2 \text{ W h kg}^{-1} \text{ at } 11160 \text{ W kg}^{-1})$  [55], artemia cyst shells derived carbon  $(25.3 \text{ W h kg}^{-1} \text{ at } 93.1 \text{ W kg}^{-1})$  [56], even outperforms some star carbon materials, e.g. carbon aerogels  $(22.75 \text{ W h kg}^{-1} \text{ at})$ 262.5 W kg<sup>-1</sup>) [57], MOF-derived nanoporous carbon (10.86 W h kg<sup>-1</sup> at  $225 \text{ W kg}^{-1}$ ) [58], carbon nanotubes  $(21.1 \text{ W h kg}^{-1})$ 4650  $W \text{ kg}^{-1}$ ) [59] and hollow carbon spheres anchored on carbon nanotubes  $(11.3 \text{ W} h \text{ kg}^{-1} \text{ at } 11800 \text{ W} \text{ kg}^{-1})$  [60]. Furthermore, the assembled NPSBC//NPSBC could easily light a 1.5 V bulb (as shown the inset of Fig. 5c) due to its high energy and power density, and this



**Fig. 5.** CV curves (a, scan rate of  $0.01 \text{ V s}^{-1}$ ) of NPSBC//NPSBC at different potential windows; specific capacitance versus current density plots (b) and Ragone plot (c) of NPSBC//NPSBC at a potential window of 0–1.5 V; cycle stability of NPSBC//NPSBC at a current density of 5 A g<sup>-1</sup> (d, inset is a EIS curves of before and after 10,000 cycles).

visually demonstrates the practical value of NPSBC in energy storage. The cycle stability of NPSBC//NPSBC was evaluated by repeating the GCD test at the current density of  $5 \text{ Ag}^{-1}$ , and a high capacitance retention of 93.6% is achieved after 10,000 cycles (as shown in Fig. 5d). The inset of Fig. 5d compares the EIS curves of before and after 10,000 cycles, and similar to that in three-electrode systems, the curve is composed of a short arc, a nearly diagonal line and a nearly vertical line. The EIS spectra was fitted by software of ZSimpWin based on the electrical equivalent circuit (R<sub>i</sub>, internal resistance; C<sub>1</sub>, the EDLC; R<sub>ct</sub>, the charge transform resistance; R<sub>w</sub>, the diffusion resistance; C<sub>2</sub>, pseudocapacitance), and the results are shown in Table SI 4. From Table SI 4, the R<sub>et</sub> has a certain increase (from 1.2 to 2.0), and this may be owing to the cycling weakened the electron-donating ability of heteroatoms. However, R<sub>w</sub> has only slight charges after cycling (from 0.47 to 0.55), indicating that the unique hierarchical porous structure of the NPSBC is still very beneficial for ion diffusion even after many cycles.

## 3.3. Electrochemical performance of NPSBC as lithium-ion battery anode

Since NPSBC possesses an outstanding hierarchical porous structure and appropriate N-doping level, it is expected to be suitable as the anode material for lithium-ion battery. Therefore, a lithium-ion battery was assembled by using the NPSBC as anode and the lithium tablet as cathode. Fig. 6a shows the CV curves of NPSBC at a scan rate of  $0.1 \text{ mV s}^{-1}$  in the voltage window of 0.01-3 V. NPSBC shows a typical CV curve of carbonaceous anode materials. An obvious reduction peak at 0.36 V in the first cycle is related to an irreversible process of the formation of the solid electrolyte interphase (SEI, can prevents the continuous decomposition of electrolyte) layer. Moreover, it also corresponds the irreversible loss of some storage site for Li<sup>+</sup> within the carbon materials [61]. The almost overlapped CV curves of the next two cycles indicate the outstanding reversibility of Li<sup>+</sup> storage

performance. It should be noted that two pairs of redox peaks at 0.8/ 1.3 V and 1.6/2.4 V appear on both the 2nd and 3rd cycles, and these two pairs assigned to the Li insertion/extraction of defective sites within the turbostratic carbon walls and abundant pores of carbonaceous material, respectively [62,63]. It can be expected the high reversibility capacity caused by these redox reactions. Fig. 6b shows the discharge/charge curves of NPSBC for initial three cycles at a current density of 0.1 A g<sup>-1</sup>. Corresponding to the CV curve, the first discharge curve shows an indistinct voltage plateau sloped from 0.3 to 1 V, assigned to the formation of SEI layer and other side reactions. Furthermore, an obvious slope at 1.5-3 V is observed in the first discharge curve, attributed to insertion of lithium from pores structure of carbon material [64]. The high charge and discharge capacity of NPSBC during the first cycle are 1662 mA h g<sup>-1</sup> and 2414 mA h g<sup>-1</sup>, respectively, and the corresponding initial coulombic efficiency (ICP) is 68.8%, higher than that of reported carbon materials [64,65]. The excellent ICP is mainly attributed to the following three points: first and foremost, the superior mesoporous structure of NPSBC (positively correlated with reversibility capacity [9], which is confirmed by SI 11), which may act as the reservoirs for Li<sup>+</sup>; second, the large specific surface area of NPSBC provides sufficient interface between electrode/electrolyte for the adsorption of Li<sup>+</sup> and fast transport of ions and electrons; third, the suitable N-doped content improves the wettability and intrinsic conductivity of NPSBC, and it will further promote the fast transport of ions and electrons. Similar to CV curves, the next two cycles of discharge/ charge curves of NPSBC are almost overlapped, implying the capacity become stable and reversible after the first cycle.

To further understand the advantage of employing NPSBC in lithium-ion battery, the rate capacity of the NPSBC was studied (as shown in Fig. 6c). NPSBC delivers reversible capacities of 1610, 1210, 998, 825, 595 and 416 mA h g<sup>-1</sup> at current densities of 0.1, 0.3, 0.5, 1, 3 and 5 A g<sup>-1</sup>, respectively. Even at a high current density of 7 A g<sup>-1</sup>,



**Fig. 6.** Electrochemical performance of NPSBC as the anode of lithium-ion battery. CV curves (a) of NPSBC at a scan rate of  $0.1 \text{ mV s}^{-1}$ ; initial three cycles discharge/ charge curves (b) NPSBC measured at a current density of  $0.1 \text{ A g}^{-1}$ ; specific capacity of NPSBC at different current densities (c, inset is discharge/charge curves of NPSBC at different current densities from 0.1 to  $7 \text{ A g}^{-1}$ ); cycle stability and coulombic efficiency of NPSBC at a current density of  $5 \text{ A g}^{-1}$  (d).

the reversible capacity still reaches to  $275 \text{ mA h g}^{-1}$ , about 73.9% of the theoretical capacity of graphite (372 mA h g<sup>-1</sup>). Thus, NPSBC exhibits a superior rate capability at a fast Li<sup>+</sup> insertion/extraction speed. The cycle performance of NPSBC was investigated at a current density of  $5 \text{ A g}^{-1}$  and the results are showed in Fig. 6d. The reversible capacity of NPSBC is 467 mA h g<sup>-1</sup> in the first cycle and then gradually decreases to 375 mA h g<sup>-1</sup> after 600 cycles, and the capacity retention rate is 80.2%. Moreover, the columbic efficiency is always around 99% during cycling, indicating excellent cycle stability at high current density. Based on the above analysis, NPSBC still achieves very impressive performance in lithium-ion battery, also deriving from its microstructure. We infer that there are three main reasons. First, the large specific surface area can provide much more sites for Li<sup>+</sup> storage. Second, the N doping can enhance the electrochemical activity and electronic conductivity. Third and the foremost, the hierarchical porous structure can not only supply shortened paths for Li<sup>+</sup> diffusion, but also adjust the local volume change during cycling.

# 4. Conclusions

In summary, a superior biomass-derived carbon has been successfully prepared. The results are in accordance with our design that: i) the target sample NPSBC has the hierarchical porous structure (micro-, meso- and macro- porous structure from the KOH activation, fragment carbon and SBC, respectively); ii) NPSBC also possesses the interconnected framework derived from SBC and the suitable N content from PPy. Owing to the above microstructure and chemical composition features, the NPSBC displays high specific capacity, excellent rate capability and superior cycle stability in both supercapacitors and lithium-ion battery. We believe that the design and synthesis strategy of hierarchical porous biomass-derived carbon can be extended to other common crop wastes, and the obtained product may also be applicable in other fields, including catalyst, adsorbent and hydrogen storage due to their unique pore structure.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2018.05.061.

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