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A simple and universal method for preparing N, S co-doped biomass derived carbon with superior performance in supercapacitors



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ABSTRACT

In this work, N, S co-doped pomelo peel derived carbon is successfully prepared by a simple one-step method. The derived carbon exhibits high specific capacitance (317 F g^{-1}) and excellent rate capability (69.7% of capacitance retention at 15 A g^{-1}), owing to its large S_{BET} , high heteroatom doping rate and suitable graphitization degree (these characteristics are derived from the synergistic activation and reduction of thiourea dopant). The one-step method is applied to the other two biomasses (bamboo fiber and sugarcane bagasse). The derived carbons of the other two biomasses till show outstanding electrochemical performance due to their similar microstructure and chemical composition to pomelo peel derived carbon, which suggests the universality of the one-step method. The series of carbon materials are applied to symmetric supercapacitors, all of which show high energy density (30.6–24.6 Wh kg⁻¹), indicating the potential application of such carbon materials in energy storage.

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1. Introduction

Over the past few decades, many researchers are committed to developing new green energy (e.g., wind, solar and water [1,2]) in order to solve the fossil energy crisis and the environmental pollution caused by fossil fuels. In general, these new energies are converted into electricity for people's production and life. However, the difficulty to store these electricity converted from new energy greatly limits the further application of new energy [3,4]. Therefore, the development of efficient energy storage devices is imperative.

Symmetric supercapacitors (SSC), as a new type of electrochemical energy storage device, have caused widespread concerns owing to their high power density, excellent cycle life and rapid charge/discharge rate [5–7]. Usually, the electrodes of SSC are made of carbon materials due to their high specific surface area, rich pore structure and chemical stability [8]. As we all know, the carbon-based SSC is an electric double-layer capacitor, and it stores energy by a physical process, which is charge separation at the interface of electrode and electrolyte [9]. Thence, the energy density of SSC depends on the accessible surface area of carbon materials. Unfortunately, the surface of carbon matrix is naturally hydrophobic. It means that the accessible surface area of carbon material is very limited, though it has a high specific surface area. Hence, SSC shows the poor energy density and cannot meet the need of practical applications.

Heteroatom doping method has been considered to significantly improve the wettability and electrochemical performance of carbon materials [10,11]. Especially, N-doped carbon has been widely applied to address energy-related challenges [12–14], which is attributed to the fact that N-doping improves not only the wettability, but also the conductivity and electrochemical activity of carbon matrix [15]. Compared with N-doping, the S-doping related research is still rare. It has been reported that S-doping can cause a large shift of the Fermi level to the valence band in the carbon material [10]. This phenomenon will provide a more polarized surface, which will ensure good wettability of the carbon surface, and further promote the transfer of electrolyte ions in pore structures of the carbon matrix [16]. Hence, S-doped carbon possesses enormous potential in the field of energy storage.

Very recently, some groups have started concentrating on N, S co-doped star carbon (e.g., graphene [17], carbon nanotube [18]), and they hope that the synergistic effect of N-doping and S-doping



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can further improve the electrochemical performance of star carbon. For instance, Gopalsamy et al. have prepared the N, S co-doped graphene with cyanamide and benzyldisulphide as N and S sources, respectively, by step-by-step doping process, and the results showed that the electrochemical performance of dually doped graphene is better than that of single doped and undoped graphene [19]. The same exciting results were also found by Zhang et al. [20], Cai et al. [21], and Cheng et al. [22] with similar step-by-step doping process. However, the additional doping process will further increase the cost of the already expensive star carbon, which is obviously not conductive to the practical application of N, S codoped carbon for energy storage.

In response to the above problem, people are turning their attention to biomass derived carbon (BDC) due to the wide ranges of sources, rich in porous structures and low costs of such carbon materials [23]. Some groups have successfully prepared the N, S codoped BDC with excellent electrochemical performance, when BDC replaces star carbon and undergoes the step-by-step doping process [24]. However, the multiple doping process still hinders the practical application of N, S co-doped carbon. To solve this problem, some researchers have also selected special biomass (a biomass that naturally contains N and S) to prepared N, S co-doped BDC by one-step method. For example, Gao et al. [25] and Liu et al. [26] have prepared N, S co-doped BDC with excellent electrochemical performance by one-step method, using honeysuckles and human hair as carbon sources, respectively. Regrettably, this research idea is still not universal, based on the fact that the most common biomass, especially crop waste, does not contain N and S.

In this study, we are committed to developing N. S co-doped crop waste derived carbon (NSCWC) by a rarely reported one-step method using thiourea as the dopant. It is based on the following considerations: i) the abundant and readily available crop waste can greatly reduce the cost of raw materials for N, S co-doped carbon. ii) The facile one-step method can further reduce the preparation cost of N, S co-doped carbon. Therefore, we compare the electrochemical performance of NSCWCs produced by two methods: one-step method (NSCWC1) and step-by-step method (NSCWC2). In this study, for the first time, we find that different from the thiourea only acting as a dopant in step-by-step method, in one-step method, thiourea acts as not only a dopant but also an activator. Moreover, interestingly, NSCWC1 has a larger specific surface area and a higher heteroatom doping ratio than that of NSCWC2, which further leads to NSCWC1 exhibiting excellent capacitive performance. This synthesis method will advance the practical application of N, S co-doped carbon-based SSC.

2. Experimental section

2.1. Sample preparation

All the original biomasses (pomelo peel, bamboo fiber, sugarcane bagasse) used were collected from Fujian province (Southeast China), cut into small pieces, washed by deionized water to remove the dirt, and then dried overnight before use. For one-step method preparation of N, S co-doped BDC, taking pomelo peel as an example, briefly, 2.0 g pomelo peel pieces, 2.0 g KOH and 0.125 g thiourea (CN₂H₄S) were poured into 50 mL ethanol with stirring for 2 h, dried at 60 °C to evaporate the ethanol, and then carbonized at 800 °C (heating rate was 5 °C min⁻¹) for 2 h under Ar atmosphere. Subsequently, the resulting product was washed by 1 M HCl and water until the pH of the filtrate was 7.0. Finally, the sample was dried at 80 °C for 12 h, and denoted as NSPPC1. Similarly, bamboo fiber and sugarcane bagasse derived N, S co-doped BDC by one-step method are denoted as NSBFC1 and NSSBC1, respectively. In addition, pomelo peel derived carbon (PC, obtained by direct carbonization of pomelo peel) and unactivated N, S co-doped pomelo peel derived carbon (NSPPC, obtained by one-step method except that KOH was not added) were also prepared for comparison. Again, the NSPPC1 sample was heat-treated at 800 °C for 1 h under H₂/Ar atmosphere (the volume ratio of H₂/Ar was 1/9) to remove the surface heteroatom functional groups, and denoted as NSPPC1-R.

For preparation of N, S co-doped BDC by step-by-step method, still taking pomelo peel as an example, a typical process was as follows: first, we prepared undoped KOH activated pomelo peel derived carbon (PPC) by a method similar to NSPPC1 except that thiourea was not added. Second, the obtained PPC (about 0.41 g PPC could be obtained from 2.0 g pomelo peel) and thiourea (0.125 g) were added to the 50 mL ethanol, stirring, followed by the evaporation of ethanol and pyrolyzation at 800 °C in Ar atmosphere for 2 h. Finally, the product was washed (by 1 M HCl and water) and dried (at 80 °C for 12 h), and denoted as NSPPC2. Correspondingly, bamboo fiber and sugarcane bagasse derived undoped KOH activated BDC and N, S co-doped BDC by step-by-step method were prepared and denoted as BFC, NSBFC2, SBC, NSSBC2, respectively.

2.2. Characterizations

Scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, TECNAI F30) were employed to investigate the micromorphology and element distribution of samples. The degree of graphitization and defects of samples were confirmed by Raman spectroscopy (HORIBA Xplora, with the 532 nm Ar-ion laser). The chemical composition and valence states of samples were analyzed by X-ray photoelectron spectroscopy (XPS) and was performed on PHI Quantum 5000 equipped with an Al K α radiation source. N₂ adsorption/desorption measurements were carried out by a Micromeritics ASAP-2020 analyzer. The electrolyte wettability to PPC, NSPPC1 and NSPPC2 was observed by contact angle measurement (confirmed by a commercial drop shape analysis system, Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co. Ltd., China). The test piece was prepared by loading sample slurry (the mass ratio of sample, acetylene black and polytetrafluoroethylene was 90:5:5) was coated on a copper foil, and then dried at 80 °C for 12 h.

2.3. Electrochemical tests

All the electrochemical tests were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) in 1 MH₂SO₄ electrolyte. The preparation process of the working electrode was as following: a mixed slurry of active material (90 wt %), acetylene blank (5 wt%) and polytetrafluoroethylene (5 wt%, PTFE) was coated onto the stainless mesh $(1 \times 1 \text{ cm}^2)$. Then the electrode was dried at 80 °C for 12 h. and compressed at 10 MPa for 5 min. At first, a three-electrode system was used to identify the performance of each sample with platinum foil and saturated calomel electrode as the counter and reference electrode, respectively. Subsequently, the electrochemical performance of symmetric supercapacitors with NSPPC1, NSBFC1 and NSSBC1 as active materials, respectively, was investigated in a two-electrode cell configuration (CR2032 coin-type cell). The substantially identical electrodes were still prepared by the above described method (stainless mesh as current collector and its diameter was 12 mm), and they were separated by filter paper. Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS, were performed at the open circuit potential in a frequency range from 10 mHz to 100 kHz, with an ac perturbation of 5 mV) measurements were carried out in threeelectrode systems and the symmetric supercapacitors, respectively. The specific capacitance (C_m , F g⁻¹) of single electrode and symmetric supercapacitors based on GCD tests was evaluated according to equation (1) (Eq. (1)):

$$C_m = \frac{\mathbf{I} \times \mathbf{t}}{\Delta \mathbf{V} \times \mathbf{m}} \tag{1}$$

where I, t and $\triangle V$ are discharge current (A), discharge time (s) and potential window (V), respectively. The m (g) is mass of sample on working electrode in three-electrode system, and the total mass of sample on both working electrode in symmetric supercapacitors [27].

The energy density (E, Wh kg⁻¹) and power density (P, W kg⁻¹) of symmetric supercapacitors also based on GCD tests were obtained by Eqs. (2) and (3):

$$E = \frac{C_m (\Delta V)^2}{2} \tag{2}$$

$$P = \frac{E}{t}$$
(3)

where C_m , $\triangle V$ and t are specific capacitance, working potential and discharge time of symmetric supercapacitors, respectively [28].

3. Results and discussion

3.1. Material characterization

SEM and TEM were used to observe the micromorphology of various pomelo peel derived carbons, and the results were shown in Fig. 1. Overall, all samples exhibit a highly 3-dimensional interconnected frameworks structure (3DIFS) derived from the KOH activation, and this structure is very beneficial to electrolyte ion diffusion [24]. Differently, NSPPC1 (Fig. 1c) shows a richer porous structure than that of PPC (Fig. 1a) and NSPPC2 (Fig. 1b), which may be attributed to the activation of thiourea. To prove this inference, the micromorphology and specific surface area (S_{BET}) of PC and NSPPC were also measured by SEM and N₂ adsorption-desorption test, respectively, and the results are shown in Fig. S1 and S2. Obviously, the particle size is smaller than that of PC and S_{BET} of NSPPC larger (Fig. S1), and these results indicate to some extent that thiourea has an activating effect when the pomelo peel is carbonized. The specific activation reaction of thiourea will be



Fig. 2. Nitrogen adsorption/desorption isotherm and pore size distribution of PPC, NSPPC2 and NSPPC1.

explained in detail later. The TEM image (Fig. 1d) reveals a highlydeveloped microporous structure of NSPPC1 which will result in a large S_{BET}, and further have a positive influence on electrochemical performance of NSPPC1. Moreover, the elemental mappings of C, N, O and S in NSPPC1 are presented in Fig. 1e ~ i. The existence and uniform distribution of N and S are confirmed, revealing that the N and S elements are successfully incorporated into the carbon matrix.

The surface area and pore texture of samples were characterized by nitrogen adsorption-desorption test and the results are shown in Fig. 2, summarized in Table 1. The same as most biomasses derived carbon prepared by KOH activation [29,30], the patterns of all samples present typical type-I isotherm, which possesses a plateau at the low-pressure range, indicating a highly-developed microporous structure [31], and this result is consistence with the inference of TEM image. Interestingly, different from our usual understanding, the S_{BET} of NSPPC1 and NSPPC2 are much higher and slightly smaller than that of PPC, respectively. The same as the analysis of SEM, this phenomenon again means that thiourea acts as not only a dopant, but also an activator during pomelo peel carbonization. As for the decrease in S_{BET} of NSPPC2, it should be attributed to the pore structure collapses of PPC when PPC



Fig. 1. SEM images of PPC (a), NSPPC2 (b), NSPPC1 (c); TEM image of NSPPC1 (d); dark field TEM (e), C (f), N (g), O (h) and S (i) elemental mapping STEM images of NSPPC1.

 Table 1

 Pore structure parameters, compositions and graphitization degree of PPC, NSPPC2 and NSPPC1.

Sample	Pore structure parameters			XPS spectra analysis				Raman spectra analysis				
	$S_{BET}/m^2 \ g^{-1}$	D _{av} (nm)	$V_T (cm^3 \ g^{-1})$	C/at.%	N/at.%	O/at.%	S/at.%	I/%	D/%	D"/%	G/%	I_G/I_D
PPC	1626	2.31	0.85	90.8	_	9.2	_	37.5	27.3	24.8	10.4	0.38
NSPPC2	1450	2.13	0.70	95.3	0.8	3.4	0.5	25.1	32.2	26.4	16.3	0.51
NSPPC1	2206	2.02	1.12	91.6	2.5	4.3	1.6	40.1	26.6	21.7	11.6	0.44

undergoes pyrolysis again, and the reduced average pore size of NSPPC2 indirectly proves the above point. In general, the one-step method is beneficial to increase the S_{BET} of the NSPPC1 due to the activation of thiourea during the carbonization process of pomelo peel.

Raman spectroscopy can expose the defects and characterize the graphitization degree (GD) of carbon samples. As shown in Fig. 3a, all samples exhibit two salient Raman peaks at 1355 and 1605 cm^{-1} , assigned to the D and G bands of carbon materials, respectively. For D band, in a broad sense, it is originated from the disorder induced by the sp^3 defect sites on the graphitic plane [32]. In depth, the above brief statement reflects two aspects: i) Polycrystalline carbonaceous materials consist of large numbers of small graphitic crystallites carbon atoms at the edge of graphene-like layers [33,34]. ii) There are many heteroatoms directly adjacent to the carbon atoms of graphene-like layer due to the fact that these heteroatoms partially replace these carbon atoms [35], which means that the sample will contain a large number of graphitic N when the D band content is high for the heteroatom N. Herein, NSPPC2 contains considerable graphitic N due to its high D band content (further confirmed by XPS spectra). For G band, it is derived from the E_{2g} vibration mode present in the sp²-bonded graphitic carbon [32]. The GD of sample can be donated by the area ratio of G and D bands (I_G/I_D). Apparently, the GD of NSPPC2 is much higher than the other samples (Table 1), mainly owing to the following facts: first, the secondary pyrolysis can effectively improve the GD of carbon materials; second, thiourea can participate as a reducing agent in the secondary pyrolysis process [36,37]. Moreover, compared with PPC, NSPPC1 also exhibits a higher GD (Table 1) due to the reduction of thiourea. The Raman spectra of all samples were also fitted by I (peak at 1253 cm^{-1}) and D" (peak at 1530 cm^{-1}) band, derived from impurities or heteroatoms (for NSPPC1 and NSPPC2, it is derived from the heteroatoms of N, O and S; for PPC, it is only derived from the heteroatom of O) on the graphitic plane and the defects of graphene layer stacking, respectively [38]. For the content of I band, NSPPC1 is meaningfully larger than the other samples (Table 1), which may be based on the fact that NSPPC1 has not only a variety of heteroatom types, but also a high heteroatom content (further confirmed by XPS spectra). In short, Raman spectra reveal that NSPPC1 possesses a suitable GD at high heteroatom doping ratio, and these features will have a profound impact on its electrochemical performance.

The effect of different preparation methods on the content and valence state of O, N and S heteroatoms in samples were implied by XPS spectra. As shown in Table 1, all samples contain a certain amount of O element, which derived from KOH activation, and brings the C-OH/C=O (531.2 eV), C-O-C (532.8 eV) and O-C=O (534.2 eV) oxygen-containing functional groups on the carbon surface (Fig. S3b) [16]. Notably, the O content of NSPPC2 is significantly smaller than the other samples, which echoes the assertion of thiourea as a reducing agent in the Raman spectra analysis. Correspondingly, the C content of NSPPC2 is larger than the other samples, and the C 1s peaks of NSPPC2 and NSPPC1 can be fitted into five peaks centered at 283.7, 284.5, 285.5, 286.1 and 287.7 eV (Fig. S3a), assigned to C-S-C, C-C, C-O, C-N/C=N and C=O bond [39,40], respectively. As we expected, PPC has no signal of N element, on the contrary, NSPPC1 and NSPPC2 show a relatively obvious N element signal, and the N 1s peaks can be deconvoluted into four peaks attributed to the pyridinic N (N-1, 398.7 eV), pyrrolic N (N-2, 400.1 eV), graphitic N (N-3, 401.5 eV) and oxydic N (N-4, 404.1 eV) (Fig. 3b). The N-1 can improve the capacitive performance of carbon materials owing to it provides a pair of electrons for conjugation with the π -conjugated rings. The N-2 is a good electron-donor with highly charge mobility, which will greatly



Fig. 3. Raman spectra (a), high resolution N 1s (b) and S 2p (c) XPS spectra of PPC, NSPPC2 and NSPPC1.

promote the electrochemical reaction activity of carbon surface [41]. The N-1 and N-2 content of NSPPC1 is larger than that of NSPPC2, predicting the superior electrochemical performance of NSPPC1. Meanwhile, the graphitic N content of NSPPC2 is higher than that of NSPPC1, which confirms the inference of Raman spectra analysis. For S 2p orbits (Fig. 3c), similar to N 1s orbits, it is still not observed in PPC: however, it appears in NSPPC1 and NSPPC2, and it can be fitted into three peaks. Two peaks at 163.8 eV (S 2p_{3/2}) and 165.1 eV (S 2p_{1/2}) are constrained by 1.3 eV binding energy separation, responding to spin-orbital splitting of thiophene-like S incorporated into the carbon matrix; the other peaks at 168.4 eV are attributed to the C-SO_x-C states (e.g. sulfoxide and sulfone) [42,43]. On the one hand, compared with N element, S incorporating of the carbon matrix will increase the electron density and polarization of the carbon surface. On the other hand, sulfoxide and sulfone will bring the pseudo-capacitive behavior [44]. Of particular note, the content of N and S of NSPPC1 is much higher than that of NSPPC2 (Table 1, consistent with the inference of Raman spectra analysis), suggesting that one-step method can bring a high heteroatom doping rate, which is mainly derived from the dopant thiourea participates in the activation reaction. Furthermore, the high heteroatom doping rate will improve the wettability of carbon matrix. As shown in Fig. S4, the contact angle of NSPPC1 is significantly less than NSPPC2 and PPC, which can further promote the surface activity of NSPPC1.

Briefly, compared with the NSPPC2 obtained by step-by-step method, NSPPC1 obtained by one-step method exhibits the highly-developed microporous structure, large S_{BET} , suitable GD and high heteroatom doping ratio. These advantages can bring about predictable superior electrochemical performance, which may be mainly derived from the triple roles of thiourea (doping, reduction and activation) in one-step method.

3.2. Mechanism analysis of thiourea involved in activation reaction

In this study, NSPPC1 was obtained by carbonizing the pomelo peel, KOH and thiourea composite, followed by 1 M HCl treatment. In this process, thiourea acts not only as a dopant and a reducing agent as have been reported [36,37], but also as a synergistic activator in the presence of KOH, and this synergistic activation is rarely reported. To reveal this synergistic activation, the samples derived from one-step method were prepared at various temperatures during carbonization, and characterized by XRD spectra (Fig. 4). We can infer that the activation begins with common KOH activation reaction 1 (Re. 1) and forms a lot of K₂CO₃1.5H₂O (JCPDS No. 11-0655) [45,46] at 400 °C. Meanwhile, a certain amount of K₂N₂O₃ (JCPDS No. 36-0504) is also produced with Re. 2, which demonstrates that thiourea first reacts with KOH and then participates in the activation process. Then at 500 °C, the diffraction peak intensity of K₂N₂O₃ becomes weaker due to K₂N₂O₃ involved in the Re. 3, and this reaction will increase the S_{BET} of NSPPC1 (Re. 3 will etch the carbon framework). Interestingly, the weak diffraction peaks of KSCN (JCPDS No. 79-0160) are also discovered at 500 °C. Researches have shown that thiourea can be isomerized to NH₄SCN under heating condition (Re. 4) [37,47], subsequently, NH₄SCN will react with the residual KOH to product KSCN (Re. 5).

 $6KOH + 2C + 3H_2O \rightarrow 2K + 3H_2 + 2K_2CO_31.5H_2O,$ (1)

 $2KOH + (NH_2)_2CS + 3H_2O \rightarrow K_2N_2O_3 + H_2S + CO_2 + 5H_2,$ (2)

 $2K_2N_2O_3 + 5C + 9H_2O \rightarrow 2K_2CO_31.5H_2O + 4NH_3 + 3CO_2,$ (3)

 $(NH_2)_2CS \leftrightarrow NH_4SCN,$ (4)

KSCN 800 °C Intensity (a.u.) 700 °C 600 °C 500 °C 400 °C 70 10 20 30 2 50 60 40 80 Theta (degree)

K₂CO₃·1.5H₂O

.

Fig. 4. XRD spectra of samples derived from the one-step method preparation of N, S co-doped pomelo peel derived carbon at various temperatures in the process of carbonization.

$$KOH + NH_4SCN \rightarrow KSCN + NH_3 + H_2O,$$
(5)

 $4KSCN + 2C + 13H_2O \rightarrow 2K_2CO_31.5H_2O + 4H_2S + 4NH_3 + 4CO,(6)$

As the pyrolysis temperature increases (600–700 °C), the peak intensity of KSCN is gradually weakening. This is because KSCN also reacts with carbon framework (Re. 6) to further increase the S_{BET} of NSPPC1. Until the pyrolysis temperature reaches 800 °C, $K_2N_2O_3$ and KSCN are basically exhausted, and they eventually turned into $K_2CO_31.5H_2O$. However, for step-by-step method, thiourea will directly decompose into highly reactive N or S species such as NH₃, CS₂ and H₂S when KOH is not present, and the reduction of carbon becomes dominant under heat treatment [48]. Therefore, compared with one-step method, step-by-step method not only lacks the reaction (Re. 3 and 6) that can further etch the carbon framework, but also the direct pyrolysis vaporization loss of thiourea will reduce the heteroatom doping ratio of carbon matrix. This mechanism is a good explanation for the large S_{BET} and high heteroatom doping ratio of NSPPC2.

3.3. Electrochemical behavior of PPC, NSPPC2 and NSPPC1

The electrochemical performance of PPC, NSPPC2 and NSPPC1 were firstly studied by CV, GCD and EIS in a three-electrode system, and the results are shown in Fig. 5. Basically, the CV curves of all samples (Fig. 5a) exhibit a symmetric rectangular shape and NSPPC1 shows the maximum current response, suggesting NSPPC1 possesses the most outstanding ideal electrochemical double-layer capacitance (EDLC) behavior [49]. Moreover, a pair of weak redox peaks is observed on the CV curve of NSPPC1, indicating the limited pseudocapacitance behavior is derived from doped heteroatoms [50]. However, the redox peaks of NSPPC2 are basically invisible due to its low heteroatom doping ratio. In order to prove the above views, NSPPC1 was heat-treated again at 800 °C for 1 h under H₂/Ar



Fig. 5. CV (a, scan rate of 0.01 V s⁻¹), GCD (b, current density of 1 A g⁻¹) curves of PPC, NSPPC2 and NSPPC1; specific capacitance versus current density of PPC, NSPPC2 and NSPPC1 (c); EIS curves of PPC, NSPPC2 and NSPPC1 (d).

atmosphere (NSPPC1-R). The XPS spectra of NSPPC1-R show a significant reduction in the content of heteroatoms (Fig. S5a, Table S1), and correspondingly, its CV curve does not have any redox peaks and is more regularly in shape (Fig. S5b), indicating the pure EDLC behavior of NSPPC1-R. Moreover, the CV test current response of NSPPC1-R is reduced, which predicts that the pseudocapacitance derived from the heteroatoms has disappeared. Fig. 5b shows the GCD test of PPC, NSPPC2 and NSPPC1 at a current density of 1 A g⁻¹. In correspondence with CV curves, all samples are close to the shape of an isosceles triangle also owing to the ideal EDLC behavior. Obviously, the redox peaks on CV curve of NSPPC1 does not appear on GCD curve, however, it does not indicate the disappearance of the pseudocapacitance originating from the heteroatoms. Interestingly, the GCD curve of NSPPC1 at 0.2 A g^{-1} has a pair of slight redox peaks (Fig. S6c), which suggests that the pseudocapacitance of heteroatoms is present, but at a high current density, the heteroatom functional groups on the surface of NSPPC1 cannot sufficiently undergo the redox reaction, and this phenomenon has appeared in many studies [42,43,50,51]. According to Eq. (1), the specific capacitance of PPC, NSPPC2 and NSPPC1 are 253, 242 and 317 Fg^{-1} at 1 Ag^{-1} , respectively, which is consistent with the analysis of CV test. Moreover, compared with PPC, the increase in specific capacitance of NSPPC1 (25.3%) is less than the increase in S_{BET} (35.7%, Table 1), which is mainly due to the highly-developed microporous structure of NSPPC1 limiting its accessible specific surface area, though these microporous structures can lead to a high S_{BET} [52].

The relationship between current density and specific capacitance of samples is revealed by GCD test in the range of $1-15 \text{ A g}^{-1}$ (Fig. S7), as summarized in Fig. 5c. Significantly, the specific capacitance of NSPPC1 is much higher than that of PPC and NSPPC2

at each current density. Simultaneously, NSPPC1 also achieves high specific capacitance at a large current density $(221 \text{ Fg}^{-1} \text{ at})$ 15 Ag^{-1}), and its capacitance retention is as high as 69.7% (compared with 317 Fg^{-1} , at 1 Ag^{-1}), which is still better than that of PPC and NSPPC2 (the capacitance retentions of PPC and NSPPC2 are 59.3% and 66.9%, respectively). All of the above mean that NSPPC1 possesses excellent capacitive performance even at large current density. These superior performance of NSPPC1 should be attributed to its suitable GD, and especially, its wettable surface (derived from the high heteroatom doping ratio), which ensures electrolyte ion have enough time to diffuse into the highlydeveloped microporous structure [53]. It should be also noted that although the specific capacitance of NSPPC2 is less than PPC at low current density, its capacitive retention is higher than PPC. These phenomena are derived from the smallest S_{BFT} and the highest GD of NSPPC2, respectively, indicating that a high GC is another key factor in achieving excellent rate capability. EIS measurement was further performed for reveal the electrochemical behavior of samples, and the results are shown in Fig. 5d. The EIS curve of all samples contain a small semicircle at high frequency, a curve close to the diagonal at medium frequency and a line that is almost perpendicular to the Z' axis. These three parts represent charge transfer resistance (R_{ct}) , Warburg diffusion resistance (R_w) and almost ideal capacitive behavior [54], respectively. Intuitively, NSPPC1 exhibits the small R_{ct} and R_w, and meanwhile, possesses the optimal capacitive behavior. These results are consistent with the CV and GCD measurements. Furthermore, the intercept at the Z' axis expresses the internal resistance (R_i) derived from the carbon material resistance, electrolyte resistance and contact resistance between sample and current collector [55]. Actually, R_i just reflects the intrinsic resistance of the material after all samples experienced

the same test conditions. As can be seen from the inset of Fig. 5d, the R_i of PPC, NSPPC2 and NSPPC1 are 1.09, 1.02 and 0.97 Ω , respectively. Obviously, the R_i of samples decreases with the decrease of sample's contact angle (Fig. S4), revealing that the intrinsic resistance of material can be effectively reduced by heteroatom doping. In sum, NSPPC1 exhibits the outstanding capacitive performance owing to the three aspects: i) the additional S_{BET} from the thiourea participating in the activation process, ii) the surface wettability and slight pseudocapacitance from the high heteroatom doping ratio, and iii) suitable GD due to the reduction of thiourea.

3.4. Universality of BDC prepared by one-step method

Due to the diversity of biomasses, non-reproducibility may occur when applying a biocarbon preparation method to different biomass, and it is also a problem that plagues many researchers [56,57]. To verify the universality of one-step method, we applied this method to two other biomasses - bamboo fiber (BF) and sugarcane bagasse (SB), and correspondingly prepared BFC, NSBFC2, NSBFC1, SBC, NSSBC2 and NSSBC1. The micromorphology of these products were also observed by SEM, and the results are shown in Fig. S8. All samples shown the 3DIFS derived from the KOH activation, moreover, NSBFC1 (Fig. S8c) and NSSBC1 (Fig. S8f) possess a richer pore structure, which means a large S_{BFT}. In order to confirm this conclusion, the S_{BET} of all samples were tested by nitrogen adsorption/desorption measurement, and the results are shown in Fig. S9, summarized in Table S2. As we expected, the N, S co-doped BDC prepared by one-step method (NSBFC1 and NSSBC1) possess the largest S_{BET} than the other samples, and this result is similar to NSPPC1, which proves to some extent the universality of the one-step method when applying it to other biomasses. The XPS spectra were also performed in order to reveal the chemical composition and determine the heteroatom doping ratio in all samples. The C 1s/O 1s and N 1 s/S 2p high resolution XPS spectra are shown in Fig. S10 and S11, respectively, and the content of each element is summarized in Table S2. Undoubtedly, NSBFC1 and NSSBC1 still possess the highest heteroatom doping ratio. Furthermore, the reducibility of thiourea is also particularly significant (the O element content of NSBFC2 and NSSBC2 are significantly smaller than that of BFC and SBC, respectively).

The capacitive performance of all samples was also judged by

CV, GCD and EIS measurements, and the results are shown in Fig. 6. For CV curves (Fig. 6a and e), their shapes are similar to rectangles, and moreover, NSBFC1 and NSSBC1 also exhibit the weak redox peaks derived from the heteroatom. The specific capacitance of BFC, NSBFC2, NSBFC1, SBC, NSSBC2 and NSSBC1 are 218, 196, 286, 160, 170 and $255 \,F \,g^{-1}$, respectively, based on the GCD tests at $1 \,A \,g^{-1}$ (Fig. 6b and f). The specific capacitance of N, S co-doped BDCs prepared by one-step method is higher than or close to many of BDC reported in the literature, even, obviously better than many current star carbon materials (Table 2). The relationship between specific capacitance and current density of all samples was also investigated by GCD tests (Fig. S12). The capacitance retention of NSBFC1 and NSSBC1 are 66.4% and 66.7% at 15 A g⁻¹, respectively, and they are all less than the sample of prepared by step-by-step method (capacitive retention of NSBFC2 and NSSBC2 are 69.4% and 70.6%, respectively). This is still mainly attributed to the dominant reduction of thiourea in the step-by step method. From EIS tests (Fig. 6d and h) could obtained that NSBFC1 and NSSBC1 still show the outstanding electrochemical performance, owing to the fact that they are very close to the ideal capacitive behavior at low frequency, their R_{ct} (at high frequency) and R_w (at medium frequency) are very small, and they all possess an R_i (the Ri of NSBFC1 and NSSBC1 are 0.97 and 0.99 Ω , respectively) that is much smaller than the comparative samples.

In summary, NSBFC1 and NSSBC1 exhibit similar microstructures and chemical compositions to NSPPC1, and meanwhile, they all have the best capacitive performance compared to the comparative samples. Therefore, the above extended research demonstrates the universality of the one-step method.

3.5. Electrochemical performance of symmetric supercapacitors

In order to further clarify the superiority of the one-step method, a real symmetric supercapacitors is assembled (the active material of positive and negative electrodes are both NSPPC1, denoted as NSPPC1//NSPPC1), and its capacitive performance tests are shown in Fig. 7. The potential window is a key factor for a real supercapacitor, which can directly affect the energy and power density of device [65]. In previous studies, we found that the potential window for a carbon-based supercapacitors to work well is 0-1.5 V, when $1 \text{ MH}_2\text{SO}_4$ is used as the electrolyte [28,66]. In this work, the CV curve of NSPPC1//NSPPC1 at 0-1.5 V is shown in



Fig. 6. CV (a, scan rate of 0.01 Vs⁻¹), GCD (b, current density of 1 A g⁻¹), specific capacitance vs. current density (c) and EIS (d) of BFC, NSBFC2 and NSBFC1; CV (e, scan rate of 0.01 V s⁻¹), GCD (f, current density of 1 A g⁻¹), specific capacitance vs. current density (g) and EIS (h) of SBC, NSSBC2 and NSSBC1.

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Table 2

Comparison of the specific capacitance for previously reported biomass-derived carbon and the star carbon materials.

Carbon type	Electrolyte	Current density	Specific capacitance	Ref.
Eggshell membrane derived carbon	1 M KOH	$4.0 \text{A} \text{g}^{-1}$	$228 \mathrm{Fg}^{-1}$	[58]
Lotus pollen derived carbon	EMIMBF ₄	$1 \mathrm{A}\mathrm{g}^{-1}$	$207 \mathrm{Fg}^{-1}$	[56]
Water hyacinth derived carbon	6 M KOH	$1 \mathrm{A}\mathrm{g}^{-1}$	$273 \mathrm{Fg}^{-1}$	[59]
Prolifera-Green-Tide derived carbon	6 M KOH	$0.1 \mathrm{Ag^{-1}}$	$298.6 \mathrm{Fg}^{-1}$	[29]
Perilla frutescens derived carbon	6 M KOH	$0.5 \mathrm{A}\mathrm{g}^{-1}$	$270\mathrm{Fg^{-1}}$	[60]
Polypyrrole (PPy) derived carbon	1 M H ₂ SO ₄	$1 \mathrm{A}\mathrm{g}^{-1}$	$291 \mathrm{Fg}^{-1}$	[31]
Metal-Organic Frameworks (MOF) derived carbon	1 M H ₂ SO ₄	$1 { m mV} { m s}^{-1}$	$298 \mathrm{Fg}^{-1}$	[61]
MOF derived carbon	1 M H ₂ SO ₄	$2 \mathrm{A}\mathrm{g}^{-1}$	$270 \mathrm{Fg}^{-1}$	[62]
Graphene (GS) @ carbon nanotube (CNT) foam	6 M KOH	$1 \mathrm{A}\mathrm{g}^{-1}$	$135 \mathrm{Fg}^{-1}$	[63]
N-doped GS aerogels	6 M KOH	$0.2 \mathrm{A}\mathrm{g}^{-1}$	$197 \mathrm{Fg}^{-1}$	[64]
NSPPC1	1 M H ₂ SO ₄	$1 \mathrm{Ag^{-1}}$	$317 \mathrm{Fg}^{-1}$	This work
NSBFC1	1 M H ₂ SO ₄	$1 \mathrm{A}\mathrm{g}^{-1}$	$286 \mathrm{Fg}^{-1}$	This work
NSSBC1	1 M H ₂ SO ₄	$1 \mathrm{A} \mathrm{g}^{-1}$	$255 \mathrm{Fg}^{-1}$	This work



Fig. 7. Specific capacitance vs. current density plots (a), Ragone plot (b) and cycle stability (c, current density of 5 A g⁻¹) of NSPPC1//NSPPC1; CV curves (d) of NSPPC1//NSPPC1, NSBFC1//NSBFC1, NSSBC1 and their tandem device; photograph of three 1.5 V bulbs powered by the tandem device (e).

Fig. 7d. A pair of weak redox peaks caused by doped heteroatoms is observed on the CV curve and there is no significantly increased anodic current at 1.5 V, which indicates that the potential window of 0–1.5 V is suitable for NSPPC1//NSPPC1 [67]. The GCD tests were performed at current density of 1–10 A g⁻¹, and the results are shown in Fig. 7a. Corresponding to CV curve, the GCD curves are slightly offset from the isosceles triangle due to the pseudocapacitance. The specific capacitance of NSPPC1//NSPPC1 is 98 and 53 F g⁻¹ at current densities of 1 and 10 A g⁻¹, respectively, and the capacitance retention is 54.1%. These results reveal that NSPPC1 still possesses the superior rate capability in real symmetric supercapacitors.

The Ragone plots of NSPPC1//NSPPC1 based on the GCD tests are shown in Fig. 7b. A high energy density of 30.6 Wh kg⁻¹ is obtained with the power density of 740 W kg⁻¹ at a current density of 1 A g^{-1} . Even, the energy density is still as high as 16.5 Wh kg⁻¹ with the power density of 7453 W kg⁻¹ at a current density of 10 A g^{-1} . The value is superior to many of the reported BDC-based symmetric supercapacitors, such as willow catkin derived carbon

(21 Wh kg⁻¹ at 180 W kg⁻¹) [24], rice straw derived carbon (9.4 Wh kg⁻¹ at 250 W kg⁻¹) [68], bagasse wastes derived carbon (20 Wh kg⁻¹ at 182 W kg⁻¹) [69], poplar catkins derived carbon (19.2 Wh kg⁻¹ at 260 W kg⁻¹) [23], gelatin derived carbon (8 Wh kg⁻¹ at 17 W kg⁻¹) [65], artemia cyst shells derived carbon (25.3 Wh kg⁻¹ at 93.1 W kg⁻¹) [70], even also outperforms some star carbon materials, e.g. graphene aerogels (9 Wh kg⁻¹ at 400 W kg⁻¹) [39], nitrogen doped carbon aerogels (22.8 Wh kg⁻¹ at 263 W kg⁻¹) [71] and MOF-derived nanoporous carbons (10.9 and 7.1 Wh kg⁻¹ at 225 and 800 W kg⁻¹, respectively) [6,72]. The cycle stability of NSPPC1// NSPPC1 was evaluated by GCD tests at 5 A g⁻¹, and a 3.5% alteration is achieved after 5000 cycles (Fig. 7c), suggesting the outstanding cycle stability. The inset of Fig. 7c compares the CV curves of before and after 5000 cycles, and apparently, the redox peaks are weakened after the cycle, revealing the reduced specific capacitance is mainly due to the weakening of the pseudocapacitance originating from the doped heteroatoms.

Similarly, the symmetric supercapacitors based on NSBFC1 and NSSBC1 (denoted as NSBFC1//NSBFC1 and NSSBC1//NSSBC1,

respectively) were also assembled, and their electrochemical tests are shown in Fig. S14 and Fig. 7d. NSBFC1//NSBFC1 and NSSBC1// NSSBC1 can still work well at 0–1.5 V, as shown by the CV and GCD tests. Meanwhile, they all possess a high energy density (the energy density of NSBFC1//NSBFC1 and NSSBC1//NSSBC1 are 27.5 and 24.6 Wh kg⁻¹, respectively), indicating a huge practical value. Additionally, the three symmetric supercapacitors based on NSPPC1, NSBFC1 and NSSBC1 are connected to each other in accordance with the circuit diagram of Fig. 7e to form a tandem device. As can be seen from the CV curve (Fig. 7d), the voltage window of device has been expanded from 0 to 1.5 V to 0–4.5 V. The tandem device could easily light three 1.5 V bulbs (Fig. 7e) owing to its high energy and power density, and this further visually demonstrates the practical value of N, S co-doped BDC prepared by one-step method in energy storage.

4. Conclusions

In conclusion, a series of N, S co-doped biomass derived carbons have been successfully prepared by a simple one-step method with low-cost crop waste as precursors. The microstructure characterization and chemical composition analysis indicate that this series of carbon materials possess a highly developed microporous structure with a large S_{BET} derived from the KOH activation and additional activation of thiourea, as well as a high heteroatom doping rate and a suitable graphite degree are attributed to the thiourea participating in the activation process and the reduction of thiourea, respectively. All of these carbon materials exhibit high specific capacitance and excellent rate capability. Meanwhile, the symmetric supercapacitors based on these carbon materials all possess high energy density and superior cycle stability. Our results suggest that the one-step method in this study is a universal approach to the preparation of N, S co-doped crop waste derived carbon with outstanding electrochemical performance.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.04.087.

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