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Nitrogen and Oxygen Co-doped Hierarchical Porous Carbon Derived from Pine Mushroom Biomass for High-Performance Supercapacitor

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Due to the unique physicochemical properties, heteroatom doping of porous carbon has attracted wide attention. However, the complicated synthesis process and high cost limit its mass production. In this work, nitrogen and oxygen co-doped porous carbon materials (N-O-PCMs) derived from pine mushroom (PM) were prepared using a "one-step" carbonization and activation approach with potassium hydroxide (KOH) as active agent and at different PM/KOH mass ratios. The as-prepared hierarchical porous carbon materials are shown to not only contain rich N and O species, but also have an appropriate mesopore ratio and a narrow mesopore size distribution. Among all samples, the sample N-O-PCM-3 exhibits the largest specific surface area (935.8 m² g⁻¹), greatest total pore volume (0.56 cm³ g⁻¹), highest content of oxygen (20.1 at.%) and nitrogen (4.9 at.%) as well as optimal hierarchical porous structure. The N-O-PCMs were tested in two electrode systems using 1 M Na₂SO₄ aqueous electrolyte. N-O-PCM-3 shows an energy density of up to 35.9 Wh kg⁻¹ at 360 W kg⁻¹ and an outstanding long-term stability (89.7 % after 10,000 cycles). This work proposes a facile and low-cost method for synthesizing multiple heteroatom-doped hierarchical porous carbon for supercapacitors.

Keywords: Heteroatom, Pine mushroom, Co-doped, Porous carbon materials, Supercapacitor

1. INTRODUCTION

Thanks to their ultrahigh power density, excellent cyclical stability and superior charge-discharge rates, supercapacitors (SCs), a novel clean and efficient energy conversion and storage device [1-3], have attracted tremendous attention from both industry and academia, and are widely used in portable

electronics [4], smart grids [5] and other high-power applications [6]. Based on storage/release mechanisms, SCs are categorized as electrochemical double-layer capacitors (EDLCs) and pseudo-capacitors [7,8], with the former being defined as non-faradaic capacitors due to accumulation of charges by pure electrostatic attraction force on activated material surface without other chemical reaction, while the latter as faradaic capacitors, with the energy arising from the accumulation of charges during fast-reversible redox reaction. However, the electrode materials (electronically conducting organic polymers or transition metal oxides) of pseudo-capacitors tend to be unstable during charging/discharging process, leading to poor cycling stability and high price [9]. For this reason, EDLCs have attracted increasing attention in recent years.

The carbon-derived electrode materials have become a research hotspot in EDLCs due to their sustainability, environmental friendliness, morphology diversity, and excellent electrochemical performance. Previous studies have shown that uniform distribution of porous structures (including micro/meso/macro-pores cross-linked with each other) in carbon-derived materials can significantly improve the electrochemical performance of SCs [10, 11]. Specifically, micropores (<2 nm) afford high capacitance by providing abundant interface and sufficient active reaction sites, mesopores (2-50 nm) play the role of ion channel to shorten ion diffusion path, and macropores (>50 nm) serve as ion-buffering reservoirs [12]. Additionally, introducing typical heteroatom species, such as nitrogen (N), phosphorus (P), and boron (B), can remarkably improve the electrochemical performance by enhancing surface wettability, ameliorating the electrolyte ions accessibility and providing extra pseudo-capacitance [13-15]. It is worth noting that compared with one-type-only heteroatom doping, multiple heteroatom doping, such as O-N, N-P or O-N-S co-doping, has been shown as a facile and effective way to further tune the properties of carbon material [16-19]. For instance, Bei et al. fabricated an activated carbon with a proper content of doped N and O species from the traditional Chinese medicine medulla tetrapanacis, with its specific capacitance retention reaching approximately 84% at 100 A g^{-1} [16]. Liu et al. reported a rape pollen-derived hierarchical porous carbon prepared by S and N co-doping, which shows an energy density as high as 32.2 Wh kg⁻¹ at 0.089 kW kg⁻¹ [17].

Compared with carbon materials like graphene [20], carbon nanotubes [21], and templated carbons [22], bio-derived carbon materials are considered as promising candidates for SCs application, due to their natural porous structure and the chemical composition of biomass [23]. Therefore, a variety of bio-derived porous carbon materials have been synthesized via pyrolysis and activation of biomass-based precursors, such as bagasse [24], biowaste corncob residue [25], mangosteen peel [26], banana peel [27], shiitake mushroom [28], loofah sponge [29], ground cherry [30], mung bean husks [31], waste coffee grounds [32], elm samara [33], tea waste [34], rice wine lees [35], and mulberry leaves [36].

Pine mushroom (PM), a popular wild fungus in China [37], is a sustainable and abundant biomass resource, which is rich in crude protein, fat and fiber, thus can be utilized as a starting material for synthesis of N/O co-doped carbon. Moreover, the trace elements such as potassium and iron in the organic framework of PM can also be transformed into catalyst and porogen during the activation process [10, 35]. These characteristics endow PM with great potential for fabricating cost-effective and environmentally friendly carbon with comparable electrochemical performance. To our knowledge, this is probably the first report about the use of PM in preparation of activated carbon for SCs applications.

The N/O co-doped hierarchical porous carbon materials were synthesized by facile KOH activation of PM without other templates (Scheme 1). The synthetic strategy features the following advantages: (i) The naturally sustainable pine mushroom containing a large amount of functional groups serves as carbon precursor, (ii) the heteroatom content, specific surface area, and pore structure can be tuned by the dosage of KOH, and (iii) the prepared carbon materials not only contain rich N and O, but also have an appropriate mesopore ratio and narrow mesopore size distribution. The optimal sample N-O-PCM-3 was shown to possess a hierarchical porous structure with a large specific surface area (SSA), and a rich content of oxygen (20.1 at.%) and nitrogen (4.9 at.%). SCs with N-O-PCM-3 as the electrode material exhibit a significantly high specific capacitance, with an energy density of up to 35.9 Wh kg⁻¹ at 360 W kg⁻¹ and 89.7 % stability after 10,000 cycles in 1 M Na₂SO₄ aqueous electrolyte. The excellent electrochemical performance suggests the potential applications of the heteroatom-rich porous carbon from PM in energy storage and conversion.



Scheme 1. Schematic diagram for preparation of N-O-PCMs from PM.

2. EXPERIMENTAL

2.1 Materials

PM was purchased from Taobao (www.taobao.com; Chashuling, Jilin province, China). Potassium hydroxide (KOH, wt%>85%, Aladdin Chemistry Co. Ltd), hydrochloric acid and absolute ethyl alcohol were of analytical grade.

2.2 Fabrication of N-O-PCMs from pine mushroom

As shown in Scheme 1, PM was cleaned thoroughly by deionized water, oven-dried at 110 °C for 24 h and designated as DPM. Subsequently, the prepared DPM (10 g) was impregnated in KOH solution (400 mL), soaked overnight at room temperature and dried at 110 °C until complete evaporation of water. Next, the obtained nut-brown precursors were carbonized at 700 °C for 2 h under N₂ protection at a heating rate of 5 °C min⁻¹. Finally, the activated PM samples were immersed in dilute hydrochloric

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acid, followed by washing until neutral and drying at 120 °C for 24 h to obtain the PM derived N/O codoped porous carbons, which were named as N-O-PCM-x, where x (x=0, 2, 3, 4) indicates the mass ratio of PM to KOH. For instance, N-O-PCM-2 represents a type of carbon material prepared with a PM/KOH weight ratio of 2:1; meanwhile, N-O-PCM-0 was activated without KOH addition and used as the blank sample.

2.3 Characterization

The morphologies and crystal structure of N-O-PCMs were investigated by scanning electron microcopy (SEM, Hitachi S-2600N) and transmission electron microscopy (TEM and HRTEM, JEOL JEM-2100F). The structural properties of N-O-PCMs were characterized by a powder X-ray diffraction (XRD, Rigaku D/MAX-2500 system) and Raman spectroscopy (LabRAM, HR-800). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha) was carried out to determine the elemental compositions of the samples. The specific surface area (SSA) of N-O-PCMs was determined by the Brunauer-Emmett-Teller (BET, ASAP 2020 Plus HD88 System, Micrometitics), and the pore size distributions were analyzed by density functional theory (DFT) calculations.

2.4 Electrochemical measurement

The electrochemical measurements were performed on the same CHI760D electrochemical workstation via a three-electrode test system, including a working electrode, a counter electrode (Pt plate) and a reference electrode (Hg/HgO). The working electrodes (the mass loading density was about 3 mg cm⁻² for each electrode) were prepared as follows: first, N-O-PCM powders, acetylene black and polytetrafluoroethylene binder were mixed together at a weight ratio of 80:15:5 with an appropriate amount of absolute ethanol, followed by smearing the homogeneous paste uniformly on a nickel foam (about 1 cm×1 cm) and drying at 85 °C overnight. All measurements were performed in 6 M KOH or 1 M Na₂SO₄ electrolyte at room temperature.

In the three-electrode system, the specific capacitance (C_g , F g⁻¹) was calculated by the galvanostatic charge-discharge (GCD) curves using Eq. (1) [38].

$$C_{\rm g} = (I \times \Delta t) / (m \times \Delta V) \tag{1}$$

where I (A), m (g), Δt (s) and ΔV (V) are the applied current, the mass of the activated carbon material, the discharge time, and the discharge voltage range, respectively.

In the two-electrode system, the material capacitance (*C*, F g^{-1}) was calculated by Eq. (2) [31, 39].

$$C = (4I \times \Delta t)/(m \times \Delta V) \tag{2}$$

The energy density $(E, Wh kg^{-1})$ and power density $(P, W kg^{-1})$ were determined by Eqs. (3) and (4), respectively [40].

$$E = C \times (\Delta V)^2 / 7.2 \tag{3}$$

$$P=3600\times E/\Delta t \tag{4}$$

Where *m* (g) is the total mass loading of positive and negative electrodes; ΔV (V), the potential range within the discharge time; Δt (s), the discharge time.

3. RESULTS AND DISCUSSION



Figure 1. SEM images of (a) N-O-PCM-0, (b) N-O-PCM-4, (c) N-O-PCM-3, and (d) N-O-PCM-2.

Figure 1 shows the SEM morphologies of different N-O-PCM samples. In Fig.1a, N-O-PCM-0 was shown to resemble thick stacks with a smooth and flat surface, but hardly any obvious pores. However, after chemical activation, N-O-PCM-4 (Fig. 1b) was seen to have accessible macropores randomly distributed over carbon walls, which can be ascribed to the strong chemical etching reactions between KOH and carbon atoms (Eqs.5-9) [41]. In Fig. 1c, N-O-PCM-3 was observed to possess a cross-linked 3D skeleton with well-developed porosity and thin walls. These results demonstrate that PM-derived carbons were further activated by adequate KOH. The rough surface with thin walls can significantly increase the SSA of the carbon material, with more defect sites being introduced into the carbon lattice during pyrolysis, thus facilitating electrolyte diffusion. Interestingly, N-O-PCM-2 presents a large collection of irregular broken block particles with a coarse surface (Fig. 1d), probably due to the destruction of etching pores induced by high KOH dosage.

$2C + 6KOH \rightarrow 2K_2CO_3 + 2K + 3H_2$	(5)
$K_{2}CO_{2} \rightarrow K_{2}O + CO_{2}$	(6)

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{6}$$

$$K_2CO_3 + 2C \rightarrow 2K + 3CO \tag{7}$$

$$C + K_2 O \rightarrow 2K + CO \tag{8}$$

(9)

$C+CO_2 \rightarrow 2CO$



Figure 2. TEM images of N-O-PCM-3.

The N-O-PCM-3 nanostructures were further investigated by TEM. Fig. 2a shows the mesopores and macropores resulting from the etching of KOH, with a micropore-dominated surface being observed in the high-resolution TEM image without distinct lattice fringes (Fig.2b), indicating a positive effect of its amorphous nature on fast ion diffusion in SCs [36]. Besides, the amorphous nature of N-O-PCM-3 can also be demonstrated by the selected area electron diffraction (SAED) pattern (inset of Fig. 2b). The SEM and TEM results demonstrate that N-O-PCM-3 possesses the multi-level pore distribution from micro to macro scale and a hierarchical porous structure, which favors fast ion and charge transfer when used as an electrode material for supercapacitors.



Figure 3. XRD pattern (a) and Roman spectrum (b) of N-O-PCMs.

The crystallinity of N-O-PCMs was determined by XRD (Fig.3a). In the XRD patterns, there are

two broad signals at around 24° and 44°, corresponding to the (002) and (100) spacing of the graphene stacks, respectively [27], indicating the amorphous characteristics of the prepared N-O-PCMs [42]. Particularly, the intensity of the diffraction peaks at 44° decreased in N-O-PCM-2, N-O-PCM-3 and N-O-PCM-4, demonstrating lower graphitization degree after activation.

Fig. 3b shows the Raman spectra of N-O-PCMs. There are two peaks at around 1357 cm⁻¹ and 1590 cm⁻¹, which are ascribed to the D-band (disorder and structural defects) and G-band (graphitic) of carbons, respectively [24]. The D band could be derived from N/O heteroatoms doping and chemical activation of PM [43]. The defect sites in N-O-PCMs were evaluated by the intensity ratio of D band and G band (I_D/I_G) (Fig.3b), with a higher I_D/I_G value for each of the three porous carbon materials activated by KOH than that of N-O-PCM-0 (0.86), indicating a reduction of graphitization degree after chemical activation. Additionally, the I_D/I_G ratio showed an increase from 0.91 for N-O-PCM-4 to 1.02 for N-O-PCM-3 with increasing KOH/PM weight ratio, implying the generation of more defect sites with the increase of activator dosage in the chemical activation. Moreover, the I_D/I_G ratio is higher than 1 for N-O-PCM-3, indicating the presence of a large number of disordered and defect sites [44]. With a further increase of activator dosage, the pores created by KOH etching are destroyed, and the graphitized carbon is retained due to its stronger π - π conjugation, leading to a low I_D/I_G value for N-O-PCM-2 (0.93) [45]. These results are consistent with the SEM and XRD observations.

Sample	Pore structure parameter				Chemical composition (at.%)			
	Sample	$\frac{\text{SSA}}{(\text{m}^2 \text{ g}^{-1})}$	V_{micro} (cm ³ g ⁻¹)	$\frac{V_{meso}}{(cm^3 g^{-1})}$	$\frac{V_{total}}{(cm^3 g^{-1})}$	С	0	N
	N-O-PCM-0	29.9	0.0084	0.0616	0.0740	85.9	10.4	3.7
	N-O-PCM-2	790.9	0.1373	0.2930	0.4478	81.2	17.4	3.2
	N-O-PCM-3	935.8	0.1049	0.4428	0.5614	75.0	20.1	4.9
	N-O-PCM-4	855.8	0.2004	0.2622	0.4816	78.2	17.4	4.4

Table 1. The chemical composition and pore structure parameters of N-O-PCMs.

Table 2. The content of O/N functional groups evaluated from XPS.

Comple	N configuration (%)				O configuration (%)			
Sample	N-6	N-5	N-X	-	C=O	С-ОН/С-О-С	-C-O	
N-O-PCM-0	20.9	64.6	14.5		24.9	63.5	11.6	
N-O-PCM-2	6.4	65.3	28.3		9.9	71.1	19.0	
N-O-PCM-3	11.0	70.9	18.1		18.4	74.7	6.8	
N-O-PCM-4	16.1	73.3	10.6		17.5	75.1	7.4	



Figure 4. XPS survey spectra (a) and N 1s, C 1s and O 1s regions (b-d) of N-O-PCMs.

The contents of C, O and N elements in the four carbon materials were investigated by XPS (Fig. 4a). In the XPS spectra of N-O-PCMs, the three peaks at around 284.8, 400.4 and 532.6 eV represent C1s, N1s and O1s, respectively [16]. Table 1 shows the atomic contents of nitrogen and oxygen in N-O-PCMs synthesized at different PM/KOH mass ratios. N and O groups are of great importance to the electrochemical properties of SCs, and N-O-PCM-3 shows a higher heteroatom content and a larger SSA than other samples, indicating its better electrochemical behavior.

The chemical composition of the C/O/N atoms was determined by deconvoluting the peaks into several components using XPS peak software. The N1s spectrum was decomposed into three peaks: pyridinic N (N-6, 398.3 eV), pyrrolic N (N-5, 400.3 eV) and oxidized N (N-X, 402.5 eV) (Fig. 4b) [16]. N-6 and N-5 are reported to participate in reversible faradic redox reaction and induce the pseudocapacitive effect [14]. Table 2 shows the relative concentrations of nitrogen-containing groups, and N-O-PCM-3 was seen to have a high percentage (81.9%) of pyridinic N and pyrrolic N, contributing to enhance charge mobility and capacitance performance. Furthermore, compared with other biomass-derived nitrogen-containing carbons prepared by KOH activation, N-O-PCMs had smaller heteroatom loss during PM carbonization, implying the presence of structure bond between heteroatom and carbon matrix [46].

In Fig. 4c, the C 1s spectrum was shown to be fitted into four peaks at around 284.8, 285.5, 287.1 and 288.4 eV, corresponding to sp^2 C=C bond of graphitic carbon, sp^3 C–C bond, –C–OH and –C=O/–COOH bonds, respectively [17]. Figure 4d displays the O 1s XPS spectra of N-O-PCMs. The binding energy at 531.3 eV can be assigned to quinone (C=O), while the two peaks at 532.7 eV and 533.8 eV are associated with phenol (C–OH) or ether groups (C–O–C) and O=C–O bonds, respectively [47]. Previous reports [16, 48] have shown that the presence of oxygen- and nitrogen-containing groups in carbon can not only ameliorate the wettability of electrode materials, but also provide extra charge-storage sites. Therefore, the high content of redox-active N and O in all N-O-PCMs facilitates the enhancement of electrical conductivity and electrochemical capacity. In a basic electrolyte, pseudo-capacitance resulting from oxygen- and nitrogen-containing functional groups is mainly induced by the redox reactions [14, 31].

 $\begin{aligned} -C = NH + 2H^{+} + 2e^{-} \leftrightarrow -C = NH_{2} \\ -C - NHOH + 2H^{+} + 2e^{-} \leftrightarrow -C - NH_{2} + H_{2}O \\ -C - OH + OH^{-} \leftrightarrow -CO - + H_{2}O + e^{-} \\ -C = O + OH^{-} \leftrightarrow -COOH + e^{-} \\ -C = OOH + OH^{-} \leftrightarrow -COO^{-} + H_{2}O + e^{-} \end{aligned}$



Figure 5. N₂ adsorption/desorption isotherms (a) and pore size distributions (b) of N-O-PCMs.

The textural properties of N-O-PCMs were determined by N₂ adsorption/desorption tests. In Figure 5a, N-O-PCM-0 is shown to have less porous characteristics than N-O-PCM-2, N-O-PCM-3 or N-O-PCM-4, which display type IV sorption isotherms with a larger slope at lower relative pressures, confirming the generation of micropores and mesopores during chemical activation [32]. The DFT pore size distributions (Fig. 5b) further demonstrated hierarchical porous structures with a main distribution in the range of 0-4.0 nm and some meso/macro-pores within the range of 30-100 nm. It is worth noting that N-O-PCM-2, N-O-PCM-3 and N-O-PCM-4 show a significant growth of larger mesopores only in the range of 2-4 nm, suggesting a narrow mesopore size distribution. Based on the detailed pore structure parameters in Table 1, N-O-PCM-0 shows little porosity with a low SSA and a very small pore volume, while for the other N-O-PCM samples, with increasing KOH/PM weight ratio, the SSA and pore volume

exhibit an increase first, followed by a decrease, from 855.8 m² g⁻¹ and 0.49 cm³ g⁻¹ for N-O-PCM-4 to 935.8 m² g⁻¹ and 0.56 cm³ g⁻¹ for N-O-PCM-3, and then to 790.9 m² g⁻¹ and 0.1373 cm³ g⁻¹ for N-O-PCM-2. Interestingly, N-O-PCM-3 shows a much higher mesopore volume (0.4428 cm³ g⁻¹) than N-O-PCM-2 (0.2930 cm³ g⁻¹) or N-O-PCM-4 (0.2622 cm³ g⁻¹), probably due to a larger amount of mesopores. The mesopores, especially narrow mesopores, are believed to increase the available surface area for charge accumulation and provide lower-resistance ion transport pathways. Thus, N-O-PCM-3 is shown as a promising candidate for SCs due to rich micropores, an appropriate mesopore ratio with a narrow mesopore size distribution, and interconnected macropores.



Figure 6. GCD and CV curves for N-O-PCMs (**a**, **b**). GCD and CV curves for N-O-PCM-3 (**c**, **d**) at different current densities and scanning rates. Nyquist plots for N-O-PCMs (**e**). Cyclic stability for N-O-PCM-3 (**f**) (Inset: the GCD plots before and after 5000 cycles).

The electrochemical measurements were conducted first in 6 M KOH solution with a threeelectrode system. In Fig. 6a, all GCD curves of N-O-PCMs at 1 A g⁻¹ are shown to have approximately triangular symmetry, suggesting a typical EDLC behavior and good charging efficiency [38]. The C_g of N-O-PCMs are 163.7 F g⁻¹ for N-O-PCM-2 and 192.3 F g⁻¹ for N-O-PCM-4 at 1 A g⁻¹, which are far beyond commercial carbon (100 F g⁻¹). Importantly, N-O-PCM-3 exhibits the highest C_g (253 F g⁻¹ at 0.5 A g⁻¹) among all the samples, which is even higher than the value of previously reported biomass/biowaste derived carbon materials synthesized under similar conditions (Table 3). However, despite a high nitrogen and oxygen content, N-O-PCM-0 exhibits a short charge-discharge time, indicative of low C_g. This result further suggests that a significant SSA is necessary for high capacitance performance, as mentioned above. Figure 6b shows the cyclic voltammetry (CV) curves of N-O-PCMs at 50 mV s⁻¹. Apparently, N-O-PCM-3 has the maximum integral area, also indicating the largest C_g , which is consistent with the GCD measurement. Figure 6c displays the GCD curves of N-O-PCM-3 at various current densities from 0.5 to 20.0 A g⁻¹, which are typically symmetrical triangular, demonstrating excellent electrochemical reversibility. The CV curve of N-O-PCM-3 (Fig. 6d) still retains an approximately rectangular shape even at 200 mV s⁻¹, proving the dominant behavior of EDLC. A slight distortion of CV curves can be found for all N-O-PCMs, which can be attributed to the pseudo-capacitance effect induced by abundant nitrogen and oxygen functional organic groups in carbon [14].

The electrochemical impedance spectroscopy measurement was conducted in the frequency domain from 0.01 Hz to 100 kHz with an amplitude of 5 mV. In Fig. 6e, the Nyquist plots can be divided into three main regions of high, middle and low frequency, corresponding to equivalent series internal resistance (R_s), interfacial charge transfer resistance (R_{ct}) and Warburg impedance (W_z), respectively [24]. An enlarged image representing R_s and R_{ct} was inserted in Fig. 6e, with the smallest diameter of the semicircle for N-O-PCM-3, suggesting the lowest R_{ct} [9]. The equivalent circuit is displayed in the inset of Fig. 6e. The R_s values of N-O-PCM-0, N-O-PCM-2, N-O-PCM-3 and N-O-PCM-4 are 0.63, 0.84, 0.59 and 0.74 Ω , respectively. And the R_{ct} values are 42.11, 11.42, 1.97 and 6.94 Ω , respectively. Furthermore, N-O-PCM-3 shows the largest line slope at low frequency, implying an ideal double-layer behavior. The relatively low W_z and R_{ct} values of N-O-PCM-3 can be attributed to the optimized pore structure (improved mesopore ratio and narrow mesopore size distribution), appropriate N and O-doping, and improved wettability. The cyclic stability of N-O-PCM-3 was evaluated by the GCD measurement (Fig. 6f). After 5000 cycles at 10 A g⁻¹, 95.7% of its initial specific capacity can still be retained, indicating an excellent cycling durability.

Carbon source	Carbon	$C_{\rm g} ({\rm F} {\rm g}^{-1})$	Electrolyte	Ref.
Medulla tetrapanacis	Porous carbon	251/1	6 M KOH	[16]
Tea waste	Activated carbon	167/1	1 M KOH	[34]
Banana peel	Hierarchical porous carbon	206 /1	6 M KOH	[44]
Corn starch	Porous carbon	162/0.625	6 M KOH	[49]
Coconut Shell	Activated carbon	186/0.5	10 M KOH	[50]
Lotus seedpod shell	Porous carbon	165/0.5	3 М КОН	[51]
Broad beans shell	N/S dual-doping porous carbon	202 /0.5	6 M KOH	[52]
Pine mushroom	N-O-PCM-3	253/0.5	6 M KOH	This work

 Table 3. Comparison of specific capacitances between N-O-PCM-3 and biomass/biowaste derived carbon materials.



Figure 7. GCD and CV curves (a, b) of the fabricated symmetric two-electrode device in 6 M aqueous solution. SCs performance of N-O-PCM-3 in a two-electrode system using 1 M Na₂SO₄ as electrolyte: CV curves (c) at various potential windows; GCD curves (d) at different current densities; CV curves (e) at different scan rates; Ragone plots (f); Cycle-life performance (g) (Inset: the GCD curves and Nyquist plots before/after 10,000 cycles).

The practical electrochemical properties were measured in a symmetrical two-electrode device with 6 M KOH solution. In Fig. 7a, the CV curves of symmetric SC still exhibit a quasi-rectangle shape even at a high sweep rate of 200 mV s⁻¹. In Fig.7b, the GCD curves show a nearly symmetrical triangle shape at different current densities, indicating a good capacitive behavior. Moreover, N-O-PCM-3 exhibits an energy density of 12.3 Wh kg⁻¹ at 500 W kg⁻¹.

The electrochemical properties of assembled symmetric SCs were also tested in 1 M Na₂SO₄ aqueous electrolyte. Figure 7c presents the CV curves at various potential windows at 50 mV s⁻¹. It is worth noting that the CV curve had no obvious change in shape even at a broad potential window of 0-1.8 V, demonstrating a good capacitive behavior with fast charge/discharge feature.

In Fig. 7d, the GCD profiles are seen to present an almost isosceles triangle with little IR drop. All CV profiles at different scan rates are shown in Fig. 7e, and N-O-PCM-3 still retains a rectangular-like shape even at 500 mV s⁻¹. In the Ragone plots (Figure 7f), N-O-PCM-3 gives a high energy density

of 35.9 Wh kg⁻¹ at 180 W kg⁻¹ and can still reach an energy density of 10.9 Wh kg⁻¹ at 9 kW kg⁻¹, which can be attributed to the abundant oxygen-containing functional groups in the carbon material [47]. Remarkably, the power capability in this work is higher than that reported in the literature (Table 4). Moreover, the assembled symmetric device displays an excellent long-term cycling stability of 89.7 % at 10 A g⁻¹ after 10,000 cycles, as indicated in Fig. 7g. These results agreed with the GCD curves before and after long cycles. Meanwhile, the EIS curves are nearly identical for the 1st and 10,000th cycles, further confirming the excellent long-term cycling stability (Inserts of Fig. 7g).

The good electrochemical properties of N-O-PCM-3 can be assigned to the combined effect of well-grown porous structure and abundant N/O containing groups. First, the interconnected structure coupled with a relatively high SSA, suitable mesopore ratio and narrow mesopore size distribution can facilitate the rapid diffusion and adsorption of the electrolyte ion, leading to low charge-discharge resistance as well as superior capacitance performance and good cycling durability. Second, N/O co-doping can produce pseudo-capacitance by creating diverse reaction sites and defects, giving rise to acceleration of charge accumulation and an increase in capacitance.

Carbon source	Carbon	Energy density (Wh kg ⁻¹)	Ref.
Bagasse	Carbon aerogel	19.7 at 500 W kg^{-1}	[24]
Mung bean husks	Porous carbon	20.4 at 872 W kg^{-1}	[31]
Waste coffee grounds	N-doped porous carbon	11 at 7500 W kg ^{-1}	[32]
Cellulose acetate	N-doped porous carbon	21 at 750W kg^{-1}	[40]
Soybean	N-doped porous carbon	$12.5 \text{ at } 450 \text{W kg}^{-1}$	[41]
Cucumis melo fruit peel	Activated carbon	29.3 at 280W kg^{-1}	[43]
Fruit grain orange	Porous carbon	14.1 at 140 W kg ^{-1}	[53]
Waste soybean	N/O co-doped carbon	22.1 at 875 W kg^{-1}	[54]
Pine mushroom	N-O-PCM-3	35.9 at 360 W kg^{-1}	This work

Table 4. Power capability of N-O-PCM-3 sample in this work and comparison with other biomassderived carbon materials.

4. CONCLUSION

In summary, N-O-PCMs were synthesized by activation of an easily available precursor of pine mushroom and the mass ratios of PM/KOH were found to have a direct impact on the heteroatom content, specific surface area, and pore structure. The carbon materials prepared by sole activation of PM with KOH were identified to not only contain abundant N and O atoms, but also have an appropriate mesopore ratio and a narrow mesopore size distribution. The optimal sample N-O-PCM-3 was demonstrated to possess a large SSA (935.8 m² g⁻¹), a large total pore volume (0.56 cm³ g⁻¹), a rich content of oxygen

(20.1 at.%) and nitrogen (4.9 at.%) as well as a hierarchical porous structure. Using N-O-PCM-3 as SCs electrode, a high capacitance of 253 F g^{-1} at 0.5A g^{-1} was obtained. Additionally, N-O-PCM-3 in 1 M Na₂SO₄ aqueous electrolyte delivered a pronounced energy density of 35.9 Wh kg⁻¹ at 360 W kg⁻¹ and a

good cycle performance (89.7% capacitance retention over 10,000 cycles). Our work provides a facile method to prepare biomass-derived carbon materials with high electrochemical performance.

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