N, S co-doped porous graphene-like carbon synthesized by a facile coal tar pitch-blowing strategy for high-performance supercapacitors

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1. Introduction

Electrochemical energy storage technologies are a promising strategy to deal with the energy crisis. They enable the efficient use of renewable energy (e.g., wind, sunlight, and tides). Supercapacitors as a promising candidate by virtue of high-power density, rapid charge–discharge rate, and long-term cycle life have been employed as a power source in electric devices [1–3]. Nonetheless, to achieve large-scale applications, developing high-performance and low-cost electrode materials is still a great challenge.

Carbon materials have been widely used as electrode materials because of their merits of high electrical conductivity, superior stability, and low weight. Among various carbon materials, graphene holds great advantages [4]. However, its electrochemical performance is still unsatisfactory. For example, the reported specific capacitance is far below the theoretical value of 550 F g⁻¹. Porosification is a favorable option because porous graphene possesses a large surface area and short transport pathways, which are in favor of charge storage and charge transfer [5]. As for the production cost of graphene, it currently seems less competitive than commercial carbon materials. It is highly necessary to explore cheaper raw materials and manufacturing processes.

Due to reproducibility and environmental friendliness, many researchers pay attention to biomass as the precursor of carbon materials. In addition, biomass-derived carbon materials can readily inherit the unique structure, defects, and chemical composition of biomass precursors [6,7]. However, the uneven distribution of biomass limits its industrial applications. Coal tar pitch (CTP) as a byproduct of coal tar distillation can be obtained continuously and meanwhile, features a high industrial applications. Coal tar pitch (CTP) as a byproduct of coal tar distillation can be obtained continuously and meanwhile, features a high carbon content and low cost. Meanwhile, it contains a large number of polycyclic aromatic hydrocarbons that consist of sp²-hybridized carbon and has a narrow size distribution. These properties make it possible to directly synthesize porous graphene from CTP [8]. However, traditional methods to prepare CTP-derived porous graphene-like carbon materials normally need hard templates. This increases the manufacturing cost, and a lot of acid and water are used to remove the hard templates. Here, we adopt a facile coal tar pitch-blowing strategy using a novel blowing agent to synthesize an N, S co-doped porous graphene-like carbon (NSPC) material and employ it as the electrode material of supercapacitors. The porous property provides abundant active sites and short diffusion pathways for charge storage and transfer. The heteroatom doping not only accelerates charge transfer but also provides extra pseudo-capacitance [9]. Compared with single heteroatom doping that
improves merely one aspect of performance, dual-doping can improve the overall performance of materials owing to the synergetic effect [10]. We take investigate its electrochemical properties as the electrode for the large-scale production of electrode materials with superior electrochemical performance and economic benefits.

2. Experimental section

CTP and (NH₄)₂SO₄ were mixed with a mass ratio of 1:5, and the mixture was pre-oxidized at 200 °C in air. Carbonization was conducted at an Ar atmosphere (50 mL min⁻¹) and heated for 2 h at a temperature sequence of 300, 500, and 1000 °C. The obtained black powders were labeled as NSPC. Afterward, NSPC was activated by KOH at 800 °C, namely a-NSPC. The direct carbonization CTP (DC-CTP) was prepared by the same condition without adding (NH₄)₂SO₄ and KOH. The properties of CTP and characterization information are given in Supporting Information.

3. Results and discussion

Fig. 1 illustrates the preparation procedure of NSPC and a-NSPC. (NH₄)₂SO₄ was used as a blowing gas source to produce a bubbly structure and well mixed with CTP via ball-milling. The mixture was first pre-oxidized at 200 °C in air, where CTP gradually hardened and reduce its fluidity. Subsequently, (NH₄)₂SO₄ decomposed into NH₃ and SO₂ during the high-temperature carbonization up to 1000 °C, and the released gases created thin-walled bubbles within the mixture. At the same time, NH₃ and SO₂ acted as the doping sources of N and S, hence forming an N and S co-doped carbon material with a porous graphene-like structure (NSPC) at the end of carbonization. Afterward, NSPC was further activated by KOH at 800 °C to increase BET-specific surface area and microscale pore content. Thermogravimetric (TG) was used to confirm the effect of (NH₄)₂SO₄ (Fig S1). The major thermal decomposition takes place at 250–450 °C, indicating that (NH₄)₂SO₄ was not decomposed by pre-oxidation treatment and plaid a foaming role in the subsequent carbonization process.

The morphology characterization of the samples was performed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Both samples exhibit multi-porous structures with different sizes (Fig. 2a and b). The unique porous structure originated from the gases released from the decomposition of (NH₄)₂SO₄ during the carbonization process. A close observation of the TEM images with a higher magnification reveals that NSPC features a great number of bubble-like structures with thin graphene layers in a diameter range of 50–100 nm (Fig. 2c and d). Notably, the unique structure was preserved after the KOH activation and a-NSPC possesses more porous compared with NSPC. The phenomenon of the interconnected 3D porous network could be beneficial for the fast ion transfer and the infiltration of electrolytes [11]. Owing to plenty of the materials are initially stored in the interconnected ion-buffering reservoirs and the few-layer graphene walls around them are covered by it, providing a quick supply and short diffusion distance [12]. The porous structures were further characterized using N₂ adsorption–desorption isotherms (Fig. 2e and f). As shown in Fig. 2e, both samples exhibited a sharply increased adsorption capacity at low relative pressures and an obvious hysteresis loop at a relative pressure between 0.5 and 1.0, indicating a similar micropore-dominated structure with a certain amount of mesopores [13]. a-NSPC had a higher N₂ adsorption capacity than NSPC, indicating that it possessed abundant micropores [14]. Generally, micropores (<2 nm) are beneficial for enhancing charge storage, and mesopores (2–50 nm) can facilitate ion transfer [15]. The results of the pore size distribution (Fig. 2f) confirm that both samples have a large number of micropores and mesopores, but a-NSPC possesses a higher micropores and mesopores pore volume. Meanwhile, the specific surface area of a-NSPC is over two times larger than that of NSPC (2326.3 vs. 1119.4 m² g⁻¹, Table S2), activation is conducive to the formation of micropores, which causes the increase of BET-specific surface area for the porous carbons. More micropores can provide sufficient active sites for redox reactions, and rich mesoporous/macroporous channels can shorten the distance of ion transport and facilitate electron/charge transfer [16]. Thus, the high specific surface area with reasonable pore size distribution is in favor of fast redox reaction and charge transfer [17,18].

The Raman spectra of both samples show the characteristic D-band at 1350 cm⁻¹ and G-band at 1590 cm⁻¹ (Fig. 3a). Notably, the Ip/Ip′ ratio of a-NSPC and NSPC are 1.12 and 1.11, respectively. The Ip/Ip′ ratio normally increases after KOH activation [19,20], but lower the content of heteroatom doping, which may cause the reduction of the Ip/Ip′ ratio [21,22]. Therefore, the slight change may be due to the KOH activation and the decrease of heteroatom doping level. As seen from the X-ray diffractometry (XRD) patterns (Fig. 3b), there are two humps centered around 23° and 43°. Similar results of a-NSPC and NSPC reveal the amorphous structure and preserved C frameworks after the KOH activation [23]. The X-ray photoelectron spectroscopy (XPS) survey spectra are shown in Fig. 3c. They clearly show C, N, S, and O elements (Fig. 3c), and the detailed element contents are summarized in Table S3 [24]. In DC-CTP, there are only a small amount of N and S elements (Fig. S2). As for NSPC and a-NSPC, during the KOH activation process, the reaction between C and KOH at a high temperature under an inert atmosphere is responsible for the micropores formed. The sharp decrease for the N and S heteroatoms content indicates these bonds of C atoms and heteroatoms were broken with the process of KOH activation [25]. In addition, a-NSPC showed a decrease of N and S contents while an increase in O content. It was caused by KOH corrosion. The introduction of heteroatom (N and S) could be helpful to increase the capacitance by reversible redox reactions and enhance electrode surface wettability [26]. And the appropriate and more proportion of oxygen groups (including C=O and...
C–O) is beneficial for capacitance promotion [27]. The high-resolution C 1s spectra of the samples (Fig. 3d) can be deconvoluted to four peaks at 284.4, 285.4, 286.6, and 288.6 eV, respectively, corresponding to C–C, C–N, C–S, and C=O bonds, respectively [28]. In high-resolution N 1s spectra (Fig. 3e), four peaks can be attributed to pyridinic N (398.1 eV), pyrrolic N (400.3 eV), graphitic N (401.1 eV), and pyridine N oxide (403.2 eV) [29]. Interestingly, the pyridine N and pyrrolic N peaks are reduced after the activation by KOH, while the graphitic N peak is well maintained; these results illuminate that the C atoms around pyridinic-N and pyrrolic N species, mainly located at the defect sites caused by reactions with KOH, and give priority to form microporous structure [30]. These results also indicate that pyridine N and pyrrolic N are more active than graphitic N [31,32]. Fig. 3f shows high-resolution S 2p spectra, the peaks at 163.9 and 165.0 eV are related to thiophene S 2p_{3/2} and thiophene S 2p_{1/2} (such as C–S–C and C–S bridges). The band at 168.6 eV is attributed to oxidized S such as C–SO_{x–C} (x = 2, 3, or 4) [33]. After the activation by KOH, the content of oxidized S increased, but the specific value of thiophene S 2p_{3/2} and thiophene S 2p_{1/2} have not changed. This means the S atoms in neutral form were either consumed or altered into the oxidized sulfur during the KOH activation [32]. The XPS results confirm the incorporation of N and S into the C frameworks successfully and these heteroatoms still can be survived after the activation.

Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) measurements were used to evaluate electrochemical performance.
Fig. 4. (a–b) CV curves at various scan rates, (c–d) GCD curves at various current densities, (e) capacitance at different current densities, and (f) capacitance retention at 1 A g$^{-1}$ of NSPC and a-NSPC electrodes.

(Fig. 4) and Fig. 4b show the CV curves at different scan rates of 5, 10, 20, 50, and 100 mV s$^{-1}$. Their CV curves exhibit nearly quasi-rectangular shapes with bumps at 0 to 0.6 V, suggesting their combined capacitance from double-layer capacitance based on ion adsorption/desorption and pseudo-capacitance caused by redox reactions of doped functional groups [34]. And the CV curves of a-NSPC possess a larger area than the CV curves of NSPC owing to the desirable porous structure and large specific surface area of this sample, which suggests the high specific capacitance of a-NSPC. The shapes of the GCD curves are nearly symmetric triangular without a dramatic distortion at a current density range of 0.5–20 A g$^{-1}$ (Fig. 4c and 4d), suggesting the capacitive nature of storing charges and the great electrochemical reversibility. These symmetric triangular shapes with a slight deviation, indicating that the overall capacitance is a mixture of pseudocapacitance and electrochemical double-layer capacitance [35]. To calculate the pseudocapacitance, extended lines of the linear parts of the discharge curves have been drawn, which represent the double-layer capacitance parts of the discharge curves. Obviously, $t_D$ is the discharge time of the overall capacitance, and $t_D$ is the discharge time of the double-layer capacitance type [36]. Thus, the percentages of pseudocapacitance of NSPC and a-NSPC at the current density of 0.5 A g$^{-1}$ can be calculated to be 24.0 %, and 22.4 %, respectively. Their capacitance retentions at different current densities are shown in Fig. 4e. Under the mass loading of 15.9 mg cm$^{-2}$, the capacitance of NSPC is 136 F g$^{-1}$, while a-NSPC delivers 304 F g$^{-1}$ at 0.5 A g$^{-1}$, its retention is as high as 82.6%. More importantly, the capacitance retentions of NSPC and a-NSPC electrodes retained as high as 95.22% and 97.44%, respectively, at 1 A g$^{-1}$ after 10,000 cycles. The low cost and great electrochemical performance endow them with strong competitiveness. Also, the facile preparation method may open up an avenue toward large-scale electrochemical energy storage applications.

4. Conclusions

In this work, industrial byproduct CTP was utilized as a carbon precursor to synthesize an N, S co-doped graphene-like porous carbon via an ammonium sulfate-assisted chemical blowing strategy. Afterward, NSPC was activated by a chemical method to form a-NSPC with a high mesoscale pore content and a high surface area. Serving as electrode materials for supercapacitors, NSPC and a-NSPC exhibited capacitance of 208.6 and 368 F g$^{-1}$ at 0.5 A g$^{-1}$, respectively. Under the mass loading of 15.9 mg cm$^{-2}$, the electrode areal capacitances of NSPC and a-NSPC are 3.3 and 4.8 F cm$^{-2}$ at 20 A g$^{-1}$, respectively. More importantly, the capacitance retentions of NSPC and a-NSPC electrodes are 95.22% and 97.44%, respectively, at 1 A g$^{-1}$ after 10,000 cycles. The low cost and great electrochemical performance endow them with strong competitiveness. Also, the facile preparation method may open up an avenue toward large-scale electrochemical energy storage applications.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Data availability
Data will be made available on request.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.cplett.2023.140712.

References