A review of petroleum asphalt-based carbon materials in electrochemical energy storage

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Abstract: Petroleum asphalt, an important by-product of the petrochemical industry, has diverse applications but often suffers from low industrial added value. Because of its low cost, high carbon content, and high polycyclic aromatic hydrocarbon content, appropriate modification can increase its value and expand its energy storage applications. Current research progress on the common preparation methods of petroleum asphalt-based carbon materials, including template-assisted pyrolysis, molten salt treatment, activation, heteroatom doping, and pre-oxidation is reviewed, and its use in supercapacitors and alkali metal ion batteries, is also elaborated. Feasible solutions for the current problems with petroleum asphalt are proposed, with the aim of providing insights into its high value-added utilization.

Key words: Petroleum asphalt; Carbon materials; Preparation; Electrochemistry; Energy storage

1 Introduction

The rapid depletion of petrochemical energy fosters the rational and efficient utilization of limited resources, prompting intensified research into renewable energy sources to meet the development needs of modern society[1–2]. Electrochemical energy storage devices exhibit promising capabilities to either replace or augment fossil-based energy, attracting extensive attention from all sectors of society[3–4]. With the robust development of the electrochemical energy storage industry, market demands for energy storage electrode materials are continually increasing[5]. Carbon materials have been widely recognized as promising electrode candidates because of their structure designability, multi-scale pore size distribution, high conductivity, and favorable surface properties[6–7]. Precursors for producing various carbon materials typically include low-cost biomass, polymers, asphalt, etc. Among these, asphalt has elevated carbon content and abundant resources, stands out as a viable precursor for producing various carbon electrode materials.

Petroleum asphalt, a product of crude oil processed by atmospheric or vacuum distillation, has higher yield and different structures compared to coal tar asphalt[8–9].

At room temperature, it usually appears as a black amorphous solid or semi-solid with high viscosity, and its molecular structure is mainly composed of 2 elements, C and H, as well as small amounts of N, O, S, V, Cr and Ni[10]. According to the petrochemical industry standard NB/SH/T 0509-2010 “Four component determination method for petroleum asphalt”, asphalt can be distinguished into saturated fraction (Sa), aromatic fraction (Ar), resin (Re), and asphaltene (As) using different solvents[11–12]. The content of these 4 components together determines the physicochemical properties of petroleum asphalt[13–14]. In recent years, China’s petroleum asphalt production enterprises have continuously expanded their production capacity, predominantly for traditional fields such as infrastructure materials and fuels[15–17]. In 2023, the cumulative production of petroleum asphalt in China exceeded 37 million tons, with market demand continuing to expand. However, the conventional tech-

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Received date: 2024-06-13; **Revised date:** 2024-08-19

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niques mentioned above have lower utilization value for petroleum asphalt, limiting its application potential.

The production of carbon materials utilizing petroleum asphalt has distinct advantages: Firstly, petroleum asphalt has low hydrogen-to-carbon ratio (with the carbon mass fraction exceeding 80%) and is rich in polycyclic aromatic hydrocarbons, which facilitates an enhanced yield of carbon materials obtained after carbonization[18–20]. Secondly, petroleum asphalt is not affected by seasonal disturbances, affordable and readily available, facilitating the large-scale preparation of energy storage carbon materials[21–24]. Nevertheless, its complex chemical composition hinders the structure of the final carbon products.

The exceptional electrochemical energy storage capabilities of carbon materials are primarily attributed to their intrinsic pore structure, specific surface area, and surface chemical properties[25–28]. Accordingly, in view of the characteristics of porous carbon materials, it is necessary to explore rational structural design strategies[29–30]. In order to further construct high-performance carbon materials with tunable structures and broaden the utilization of petroleum asphalt in energy storage, this paper reviews the research progress of petroleum asphalt-based carbon materials (Fig. 1). Then, different preparation methods and their applications in electrochemical energy storage are also thoroughly analyzed. We aim to provide feasible reference ideas for the transformation of asphalt resources into clean and efficient energy storage electrode materials. Finally, the research prospects and development directions in this field are discussed.

2 Preparation of petroleum asphalt-based carbon materials

Petroleum asphalt exhibits fluidity at high temperatures, and different synthesis techniques can be used to modify the asphalt precursor. For example, deep activation pore formation or heteroatom doping can improve its pore size distribution and surface properties, achieving directional control of material morphology and pore structure during preparation[31–32]. In addition, petroleum asphalt, abundant in polycyclic aromatic hydrocarbons, can easily form highly ordered graphitic structures through direct carbonization[33]. However, its regular structure and small interlayer spacing result in low energy storage capacity. Pre-treatment methods such as chemical cross-linking or air pre-oxidation can change its microstructure and hinder the growth of graphite-like structures during pyrolysis and carbonization, thereby achieving its structure modification toward high value-added utilization[34–35].

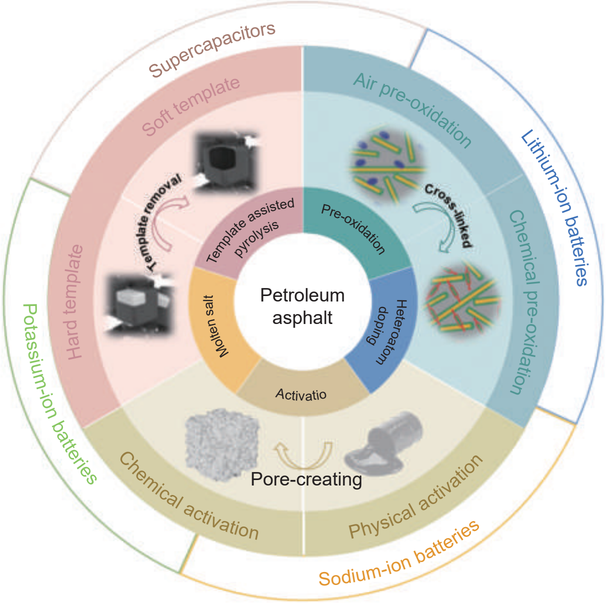

Fig. 1 Schematic illustration of synthesis strategy of petroleum asphalt-based carbon and their applications in electrochemical energy storage

2.1 Template-assisted pyrolysis method

Petroleum asphalt will melt and become plastic when heated to its inherent softening point temperature. Pyrolysis is a common way to prepare carbon materials from petroleum asphalt. In early research, low-cost asphalt and resin materials are usually directly pyrolyzed to prepare amorphous carbon materials with certain electrochemical performance[36]. Nevertheless, the direct pyrolysis of petroleum asphalt often leads to an underdeveloped pore structure and challenges in controlling the product structure, making it difficult to meet the demands of high-performance energy storage. Consequently, template-assisted pyrolysis method can rely on additives as templates to assist the pyrolysis of petroleum asphalt, inheriting template characteristics to modify the structure and morphology of the obtained carbon materials[37–38].

2.1.1 Hard template methods

Hard template method is effective for achieving controlled pore size and morphology of petroleum asphalt. The main principle is to mix asphalt into the pores or surfaces of hard template particles through physical or chemical techniques, followed by high-temperature pyrolysis and template removal to obtain asphalt-based porous carbon materials with desired morphology and size[39–40]. Specifically, during pyrolysis, when the temperature approaches the softening point, the asphalt transforms from a solid state to a semi-molten state, enveloping the template particles. As the temperature continues to rise, asphalt undergoes cross-linking and solidification reactions. After carbonization, the template agent is completely removed through physical or chemical treatments to obtain ordered porous carbon materials[41].

For example, Liu et al.[42] used nano-Fe_2O_3 (ca. 30 nm in diameter) as a hard template and petroleum asphalt as a carbon source to perform thermal decomposition treatment to the mixture (Fig. 2a-b). Then, after acid washing to remove the template, nano Fe_3O_4/petroleum asphalt-based carbon (Fe_3O_4/PC) composite materials were prepared. During the pyrolysis process, Fe_2O_3 not only acts as a template to generate pores but it is also reduced to Fe and Fe_3C species. This indicates that the structural effects caused by the reaction with carbon should be considered when selecting the template agent.

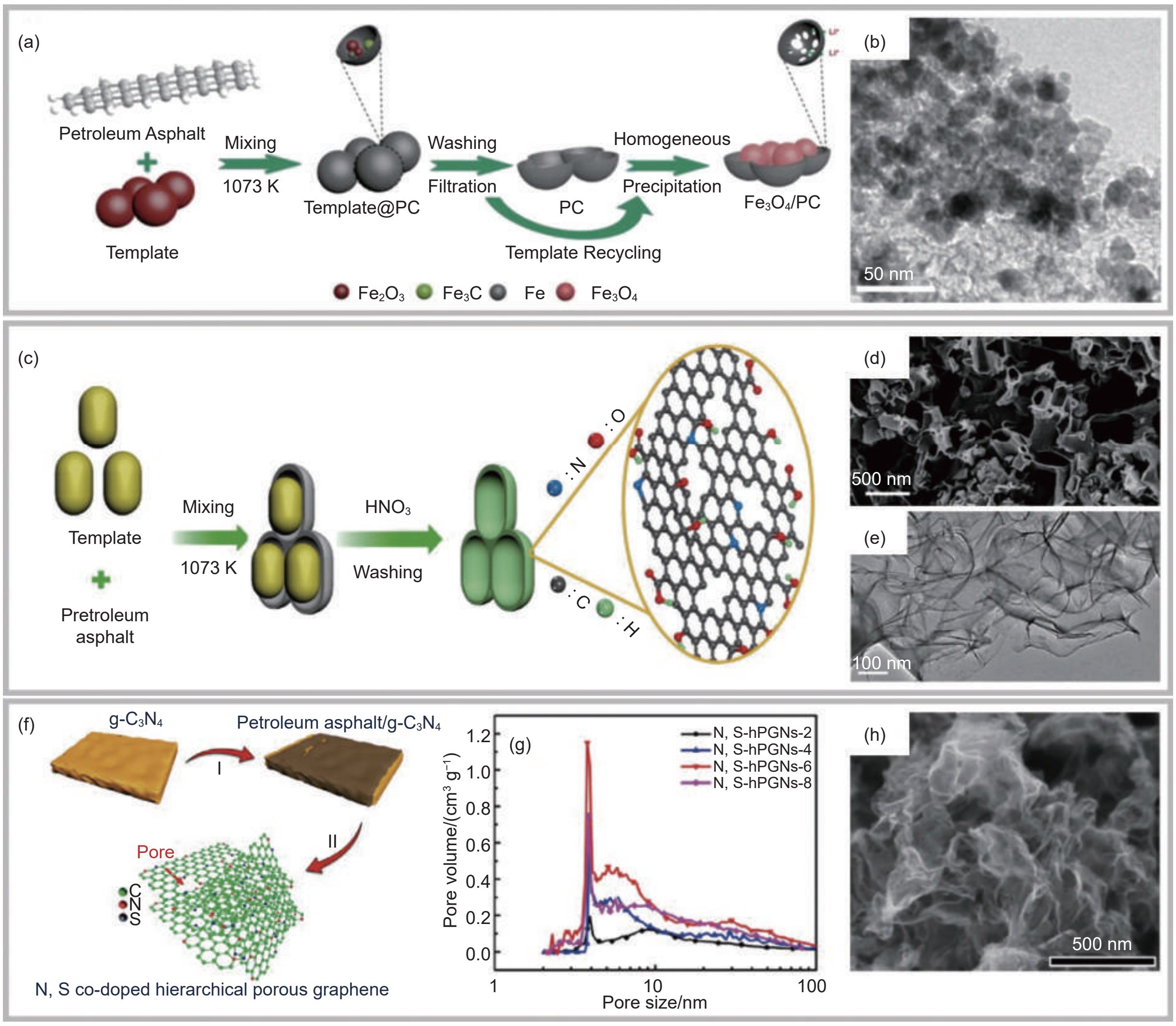

Fig. 2 (a) Schematic illustration on the fabrication and (b) TEM image of Fe_3O_4/PC nanohybrids by recyclable template strategy[42]. Synthesis schematic for (c) PACS, (d) SEM image and (e) TEM image of as-prepared PACS[43]. (f) Schematic illustration of N,S-hPGNs synthesis strategy. (g) Pore-size-distribution curve of different N,S-hPGNs-x samples. (h) SEM image of N,S-hPGNs-6[46]. Reprinted with permission

Similarly, Li et al.[43] fabricated an ultrathin hollow carbon shell from petroleum asphalt (PACS) by using a zinc oxide hard template-assisted method (Fig. 2c-e). Due to the template's steric hindrance effect, the hierarchical structure of hollow and ultra-thin carbon shells greatly shortens the diffusion path of Li^+, allowing for large lithium ion storage capacity beyond the general intercalation and surface adsorption mechanism, and promotes the rapid distribution of ions and electrolytes. Besides, the large pores brought about by template pyrolysis serve as the reservoirs for the electrolyte, ensuring that Li^+ is effectively inserted into the carbon shell from both inside and outside, beneficial for lithium-ion storage and resulting in outstanding electrochemical performances. These works indicate that hard template crucially control material nanostructure and pore size, but templates removal remain a challenge.

2.1.2 Soft template methods

The soft template method is also applied to porous carbon preparation. Commonly used template agents are mostly organic molecules or supramolecules with soft structures that interact strongly with the asphalt carbon sources forming the mesopores[44–45]. This interaction allows the template agent to self-assemble with asphalt molecules to form new organic/inorganic or composite mesostructures. Moreover, during high-temperature pyrolysis, the soft template decomposes, leaving the carbon matrix, thus no additional template removal process is required to generate a pore-rich structure.

Yang et al.[46] synthesized nitrogen and sulfur co-doped hierarchical porous graphene nanosheets (N,S-hPGNs) from inexpensive petroleum asphalt using a bifunctional graphite nitride carbon template (Fig. 2f-h). The introduction of carbon nitride template can produce a thin layered structure, with decomposed nitrogen-containing small molecules embedded in the carbon skeleton, and avoid additional tedious acid washing processes. The optimized N,S-hPGNs have a high capacity (302 F g^{-1} at 1 A g^{-1}). This work demonstrates that soft templates prevent carbon from aggregation, generating multi-scale pores, but the decomposition temperature of these soft templates must be considered for nanoporous carbon synthesis.

2.2 Molten salt method

Compared with traditional hard and soft template methods, the molten salt method for preparing petroleum asphalt-based porous carbon has advantages such as low cost, convenient operation, and easy control of morphology[47–48]. During high-temperature pyrolysis, the mixed molten salt system exhibits a molten state with high ion concentration and excellent ion-diffusion, which ensures sufficient contact between asphalt and mixed molten salt and facilitates rapid reaction kinetics. Alkaline earth metal chloride molten salts (such as NaCl, KCl) have the following benefits: (1) Low-cost salts have good ductility and are simple to handle; (2) They regulate the size and morphology of porous carbon material effectively; (3) Salt template can be easily removed by acid washing, with high purity product. Consequently, selecting a suitable molten salt system can obtain high-performance nanoporous carbon materials for electrochemical energy storage.

Wang et al.[49] prepared ultrathin amorphous carbon nanosheets by tuning the carbonization temperature of petroleum asphalt in the molten salt (Fig. 3a-b). The results indicate that nano amorphous carbon has larger interlayer spacing, enriching Li^+ storage active sites. Meanwhile, the graphitization of petroleum asphalt was constrained by the eutectic molten salt of potassium chloride and calcium chloride. Furthermore, the ultra-thin nanosheets show hierarchical pore distribution, enhancing Li^+ diffusion and transfer. Hence, the nano carbon materials constructed by the molten salt method achieve remarkable capacities and cycling performances. Wang et al.[50] used recyclable molten salt to mix asphalt with salts in toluene, forming a homogeneous mixture upon solvent evaporation, which produces disordered carbon nanosheets after carbonization (Fig. 3c-d). Amorphous carbon with increased interlayer space and abundant defects is beneficial for the intercalation/deintercalation of Li^+/Na^+. Two-dimensional (2D) nanosheets feature abundant micro/mesopores, ensuring sufficient interfaces and

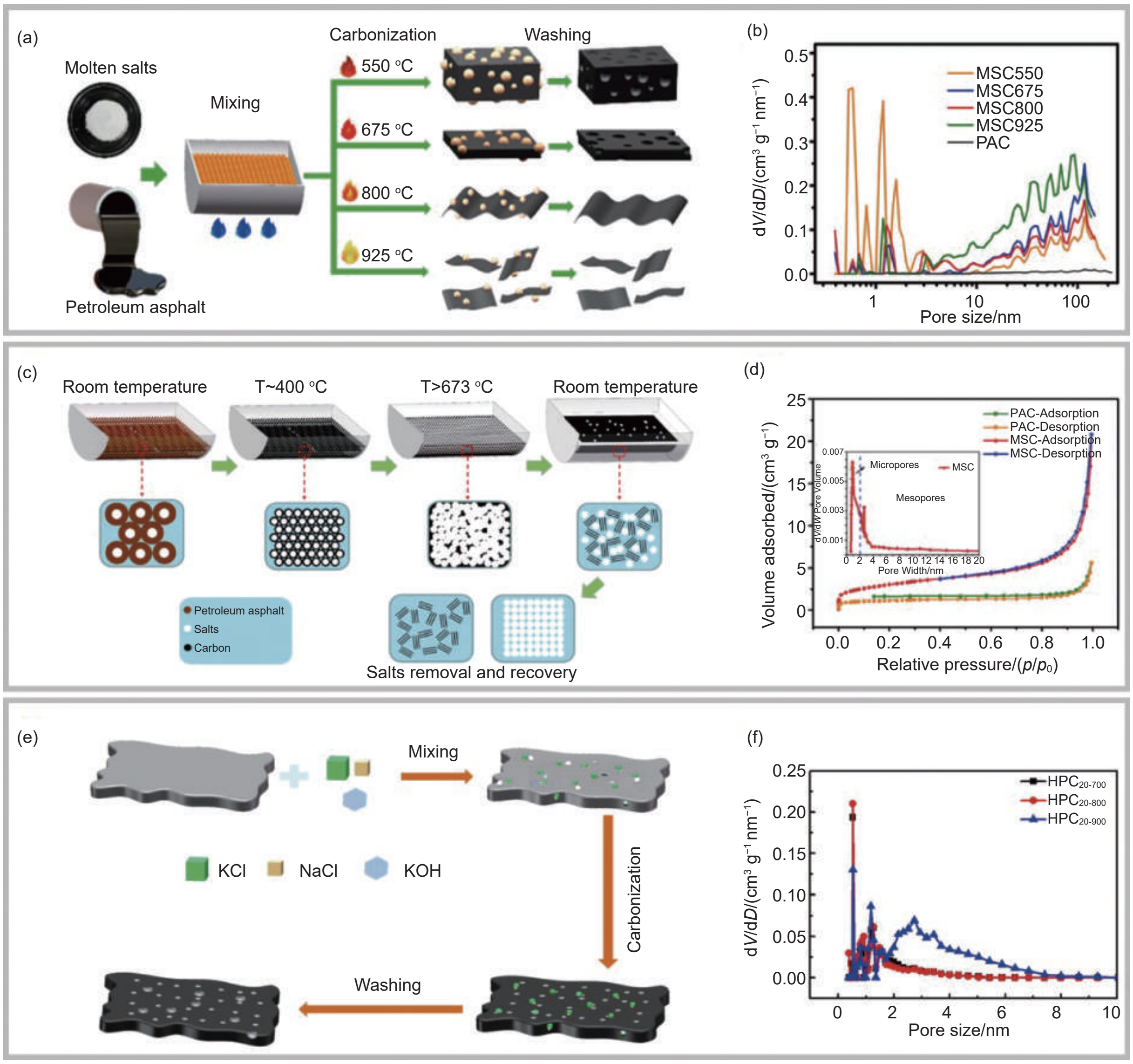

Fig. 3 (a) Schematic illustration of the evolution process of MSCs[49]. (b) Pore-size-distribution curves of different MSCs and PAC samples. (c) Schematic illustration of the preparation process for the carbon nanosheets in Molten-salt system. (d) Nitrogen adsorption-desorption isotherms of PAC and MSC with pore-size distribution (inset)[50]. Preparation schematic (e) and pore-size-distribution curves (f) of HPCs[51]. Reprinted with permission

ion transport.

Similarly, Pan et al.[51] prepared 3D interconnected honeycomb-like hierarchical porous carbons (HPCs) from petroleum asphalt by an in-situ alkali activation in molten salt (Fig. 3e-f). Utilizing the crystallization effect of molten salt to promote carbon formation, solid-phase separation is carried out to remove the molten salt and obtain carbon materials with honeycomb-shaped large pores. Molten salt acts as the reaction medium and template during carbonization, leaving pores shaped by particle distribution and volatilization. Especially, large or unevenly distributed salt particles form larger pores like honeycombs. These works demonstrate the environmental friendliness and efficiency of the molten salt method in preparing petroleum asphalt-based porous carbon. However, the issue of subsequent molten salt recovery and reuse should be considered.

2.3 Activation methods

Activation method is another classic method for forming carbon materials with pore-rich structure and large specific surface area during high-temperature carbonization of the carbon precursors[52]. According to different activation mechanisms, the preparation methods of porous carbon are mainly divided into two types: physical activation and chemical activation.

2.3.1 Physical activation

Physical activation involves the reactions between the gases such as CO_2, H_2O and H_2 and the C atoms inside the carbonaceous materials, thereby forming a more developed pore structure in the carbonized materials[53–55]. The production process of physical activation is simple, less corrosive to equipment, and does not require acid or alkali washing to obtain porous carbon materials. Guo et al.[56] prepared a 3D structured asphalt-based porous carbon with a high specific surface area (1 638 m^2/g) using air oxidation stabilization and water vapor activation processes. After pre-oxidation and carbonization of the raw materials, some small particles form stacks and pores. Notably, after water vapor activation, the number of particles increased and the particle size became uniform, resulting in an increased specific surface area. This work demonstrates that water vapor activation can effectively prepare porous carbon materials with exceptional chemical stabilities. Zou et al.[57] studied the synergistic effect of CO_2 and H_2O on the morphology and pore structure of porous carbons compared to a single activating substance. They found that CO_2 molecules mainly etch the surface of the material to obtain amorphous carbon, while H_2O molecules mainly etch amorphous carbon inside the material. Therefore, using two physical activation media can systematically activate carbon sources to obtain hierarchical porous structures.

Overall, carbon materials with a moderate specific surface area and pore volume can be obtained through physical activation methods. However, the effectiveness of these methods largely depends on how well the activation conditions match the intrinsic characteristics of the carbon sources. For example, carbon sources with poor thermal stability may experience excessive ablation, which can damage the pore structure, and result in low utilization and relatively weak reaction activity when subjected to excessively high activation temperatures.

2.3.2 Chemical activation

Chemical activation with a certain amount of chemical activators (like KOH) during carbonization is a common method for preparing high specific surface area and diverse pores petroleum asphalt-based porous carbon materials[51,58–59]. This method etches carbon with alkaline activators to prepare carbon materials with outstanding electrochemical performances. Xie et al.[60] utilized a low-cost alkaline activation strategy to combine layered porous and long-range ordered structures, producing mesoporous carbons with growth/short-range interconnections (Fig. 4a-e). The carbonization yield of pure petroleum asphalt is as high as 56.1% (Fig. 4f). Meanwhile, the comparison demonstrates that the ultra-rich pore structure is the main factor in determining electrochemical performance in low-viscosity alkaline water electrolytes (Fig. 4g). This work illustrates that, with the assistance of alkali activation agent, a high proportion of mesopores (ca. 60%) and a remarkable specific surface area (>2 000 m^2/g) of porous carbon can be obtained, resulting in excellent capacitance performance.

Furthermore, Zhang et al.[61] used potassium bicarbonate ($KHCO_3$) as an alkaline activator to carbonize potassium-containing compounds with petroleum asphalt, synthesizing porous carbon mainly composed of micropores (Fig. 4h). Light components in petroleum asphalt enhance total pore volume, favoring high surface area (1 229 m^2/g) and microporous volume (1.02 cm^3/g) (Fig. 4i-j). The advantage of this strategy is that $KHCO_3$ can mitigates the equipment corrosion and enables easy removal/recycling with water post-treatment.

In short, physical activation for petroleum asphalt-based carbon materials is cost-effective but limited in materials utilization and pore-structure control. On the contrary, chemical activation offers high materials utilization and precise pore sizes but risks pollution and equipment damage. Future studies should focus on tailored activation methods based on raw material properties for high-performance energy storage.

2.4 Heteroatom doping

Introducing heteroatoms into petroleum asphalt is another valid tactic to enhance the specific capacitance of porous carbons. Heteroatoms can effectively

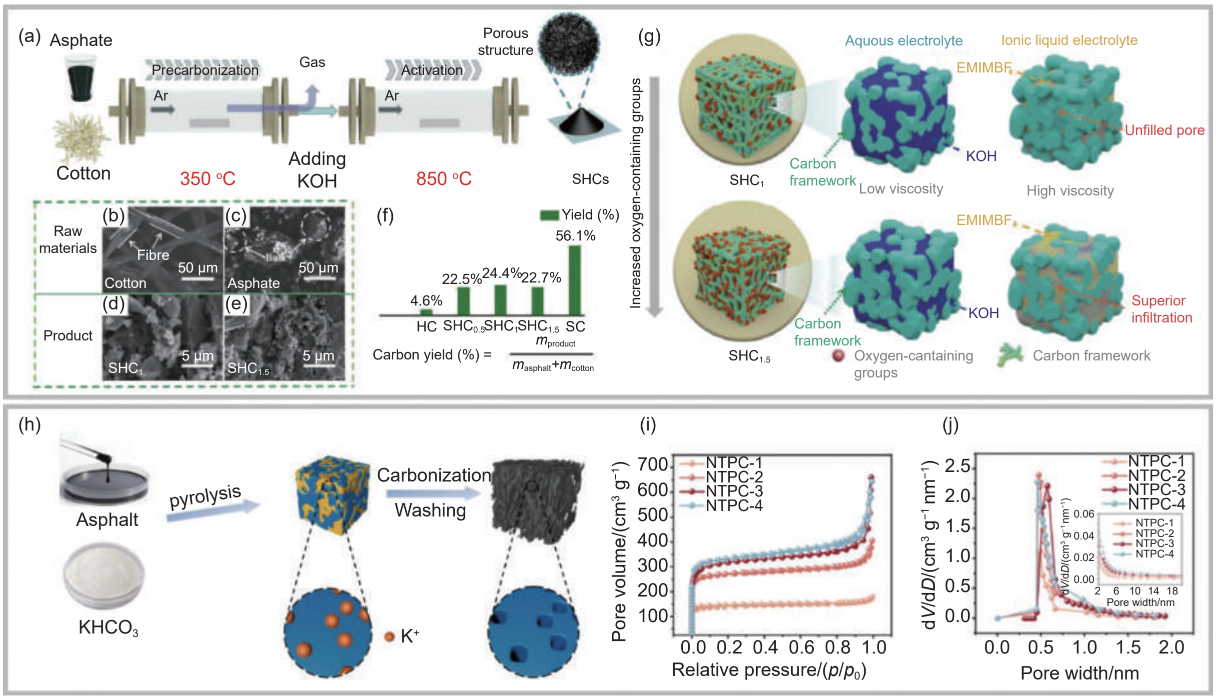

Fig. 4 (a) Schematic illustration of the preparation process for SHCs. SEM images of (b) cotton, (c) asphalt, (d) SHC_1, and (e) $SHC_{1.5}$. (f) Carbon yield of the as-made carbon samples with petroleum asphalt, cotton, and their mixture as carbon precursors, respectively. (g) Visualized distribution of two kinds of electrolytes within the pore of SHC_1 and $SHC_{1.5}$[60]. (h) Schematic illustration of the preparation process for NTPCs. (i) N_2 adsorption-desorption isotherms and (j) microporous pore size distributions (the mini diagram shows the mesopores pore size distribution) of NTPCs[61]. Reprinted with permission

induce surface polarization of carbon material structures, improve the surface properties (such as surface wettability, reduced resistance, and pseudocapacitance introduction, etc.), which further improve the specific capacitance[62–63]. Accordingly, many heteroatom-doped petroleum asphalt-based porous carbon materials have been prepared. For example, Wang et al.[64] synthesized P-doped hard carbon anode from petroleum asphalt by pre-oxidation and carbonization (Fig. 5a-d). EDS Mapping reveals a uniform distribution of elements C, O and P. The appearance of P—O bonds and P=O bonds in high-resolution XPS spectra confirms successful incorporation of P element (Fig. 5e-g). This work indicates that doping P element in hard carbon causes the structural deformation of carbon materials, expands interlayer spacing, increases internal closed micropores, and thus improves the sodium-ion storage capacity of the carbon anode.

Gao et al.[65] modified petroleum asphalt with N/P heteroatoms to create nanosheets, expanded interlayer spacing (Fig. 5h-k). Through calcination with melamine/phytic acid polymers to obtain N/P-doped carbons with high elements content. The uniform distribution of N and P elements and the presence of C—P and C—N bonds confirm successful doping (Fig. 5l-n). Through DFT calculations, it was found that the charge distribution of the pyridine nitrogen (N-6) group and phosphate group ($—C_2PO_3$) changed significantly, whereas the change in graphite nitrogen (N-Q) was relatively small (Fig. 5o). High N/P doping can effectively construct electron-rich regions, boosting the attraction of electron donors to lithium/sodium ions, and thereby improve the rate performance of the carbon materials.

These above works indicate that heteroatoms doping can improve the electrochemical performance of materials, but the potential decrease in conductivity associated with doping needs to balance. In a word, introducing various heteroatoms into carbon materials is beneficial for improving performance. Generally, introducing N atoms can introduce active sites on the surface, improving conductivity. Doping with O atoms can enhance wettability and surface properties, thereby increasing electrode energy density and catalytic activity. In addition, doping with S atoms expands the interlayer spacing of carbon, facil-

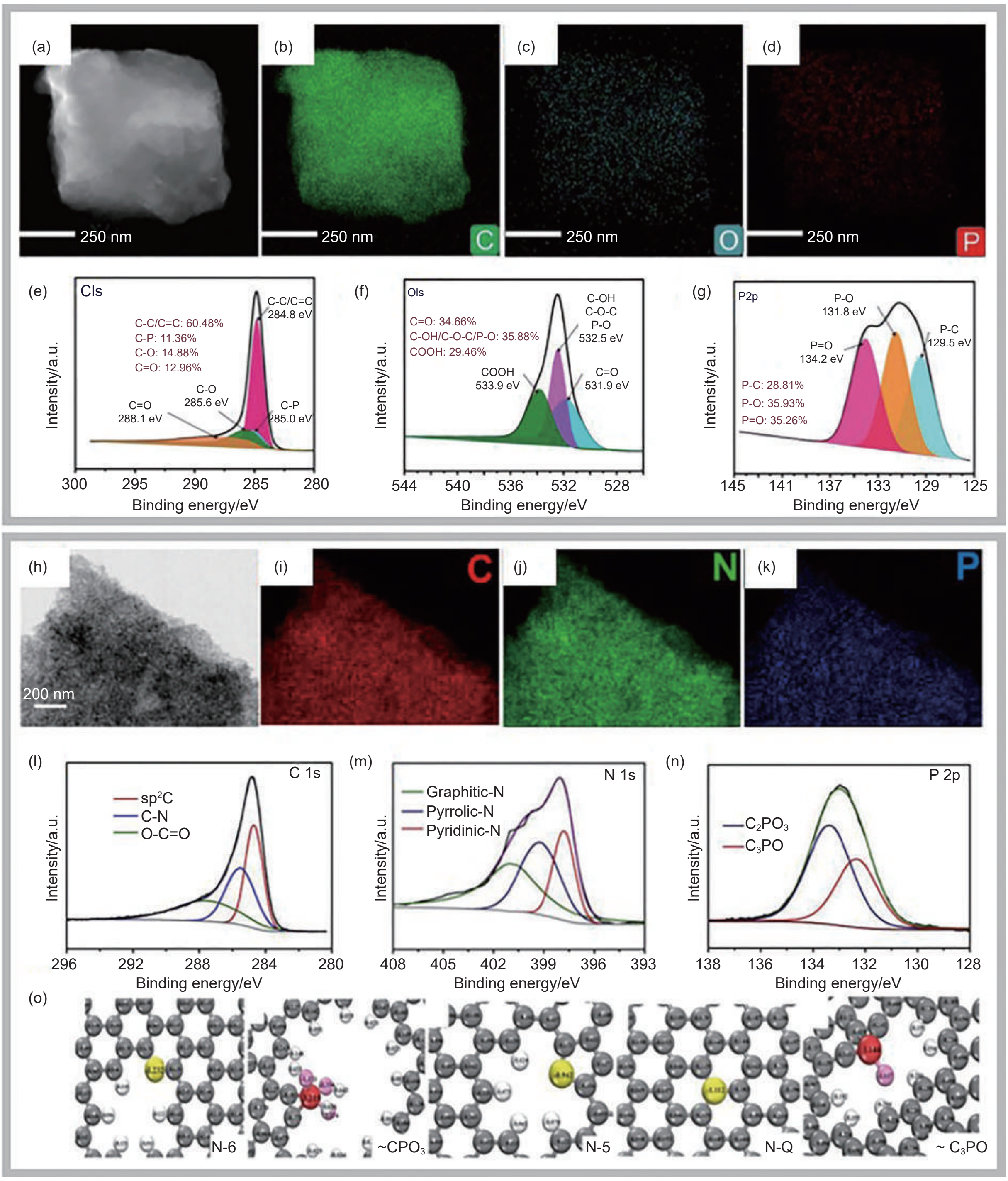

Fig. 5　(a) HRTEM-EDS mapping images of (b) C elements, (c) O elements and (d) P elements of PHC-1300. High-resolution XPS spectra for (e) C 1s, (f) O 1s and (g) P 2p of PHC-1300[64]. (h) HRTEM-EDS mapping images of (i) C elements, (j) N elements and (k) P elements of NP-CNSs. High-resolution XPS spectra for (l) C 1s, (m) N 1s, and (n) P 2p of NP-CNSs. (o) The charge distributions of functional groups containing N and P by DFT calculations (White ball: hydrogen atom; Grey ball: carbon atom; Red ball: phosphorus atom; Yellow ball: nitrogen atom; Pink ball: oxygen atom.)[65]. Reprinted with permission

itating the insertion and extraction of alkali metal ions, and thus enhancing specific capacity.

2.5　Pre-oxidation method

Direct high-temperature pyrolysis of petroleum asphalt precursors can easily form stacked structures, hindering the formation of hierarchical pore structures. Meanwhile, pyrolysis often leads to a high degree of graphitization and small interlayer spacing in soft carbon, which is not conducive to metal ion deintercalation[66–67]. For this reason, when synthesizing petroleum asphalt-based carbon materials, it is necessary to modify the pristine asphalt. The use of oxidation pretreatment can crosslink oxygen-containing functional groups with asphalt molecules, reducing material graphitization, and obtaining disordered carbon[33,68–69]. Additionally, cross-linking stabilizes the molecular structure, facilitating subsequent regulation.

2.5.1 Air pre-oxidation method

The air pre-oxidation method refers to placing asphalt in a relatively low-temperature (T < 400 °C) air environment to introduce oxygen-containing functional groups into asphalt molecules, and induce cross-linking. Xu et al.[70] explored the relationship between oxygen functional groups and carbon structure changes during asphalt carbonization by adjusting crosslinking time in pure O_2 pretreatment. The high-resolution spectrum of C 1s confirms the successful introduction of C—O and C(O)—O groups (Fig. 6a). At low temperature (250 °C), the weak thermal motion of asphalt molecules forms planar short-range ordered carbon between adjacent C—O molecules (Fig. 6b). After increasing the treatment temperature (325 °C), the thermal movement and crosslinking effect of asphalt molecules are stronger. An increase in the C(O)—O ratio is beneficial in preventing the sliding of the asphalt carbon layer and promoting the formation of disordered carbon in 3D cross-linking. Simultaneously, the pyrolysis gas can further promote the formation of closed pores and ultra-micropores, resulting in high sodium storage per-

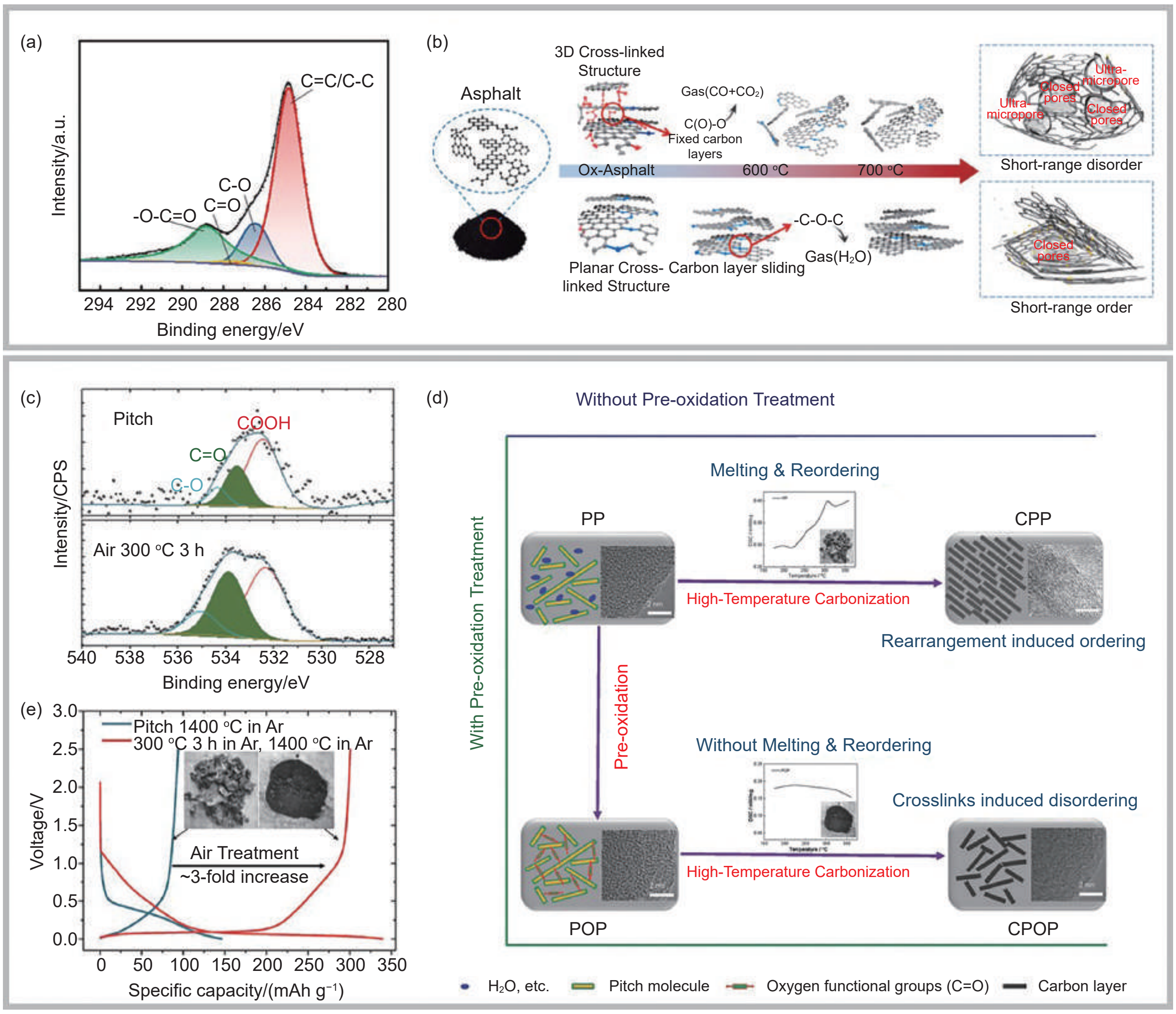

Fig. 6 (a) High-resolution XPS spectra for C 1s of 325-9 (sample cross-linked at 325 °C for 9 h). (b) The effects of the oxygen functionalities on the evolution of carbon structure during carbonization[70]. (c) High-resolution XPS spectra for O 1s of PP and POP treated at 300 °C in air for 3 h. (d) Schematic illustration of the synthesis process for carbon materials derived from unoxidized and oxidized petroleum asphalt. (e) Charge/discharge curves in SIBs[33]. Reprinted with permission formance. While oxygen pretreatment presents performance advantages, future research should focus on using safe and inexpensive air atmospheres.

For example, Lu et al.[33] realized an effective structural transformation from ordered to disordered carbon by implementing a simple pre-oxidation strategy using air, increasing the carbon yield from 54% to 67%. The introduction of oxygen functional groups at a low temperature (300 °C) prevents the melting and ordered recombination of asphalt, achieving a highly disordered structure. However, carbon derived from petroleum asphalt without pre-oxidation exhibits a long-range ordered graphitization structure. The high-resolution O 1s spectrum confirms higher C=O content in the pre-oxidized material (Fig. 6c), consistent with the structure formed by low-temperature oxidation crosslinking (Fig. 6d). The pre-oxidized modified asphalt carbon displays superior hard carbon Na^+ storage behavior, with a reversible capacity of 300.6 mAh g^{-1} and an initial coulomb efficiency (ICE) of 88.6%, outperforming the directly pyrolyzed asphalt carbon (Fig. 6e). The above work demonstrates the advantages of air/oxygen pre-oxidation, potentially promoting the commercialization of cost-effective, high-energy sodium-ion batteries (SIBs) and beyond.

2.5.2 Chemical pre-oxidation method

Apart from air pre-oxidation, chemical pre-oxidation is also a frequently-used strategy for treating asphalt precursors. This method uses strong oxidants (such as nitric acid, potassium permanganate, hydrogen peroxide, etc.) to introduce oxygen groups, facilitating cross-linking and amorphous carbon formation[71–72]. Xiong et al.[73] introduced numerous oxygen-containing ($-NO_2$) groups into petroleum asphalt carbon via nitric acid liquid-phase oxidation. The cross-linked structure effectively prevents melting and carbon layer rearrangement during asphalt carbonization, thus achieving effective structural modulation. The highly disordered carbon material prepared with wide interlayer spacing and abundant closed pores exhibits a specific capacity of 317.0 mAh g^{-1} at 30 mA g^{-1} and an attractive ICE of 88.3%. Wang et al.[74] confirmed that nitric acid oxidation introduces O/N-containing groups into asphalt, increasing its molecular weight. Compared with non-pre-oxidized soft carbon, chemically oxidized hard carbon has larger interlayer spacing and more defects, improving electrochemical performance with an appealing ICE of 79% and better long cycle stability. After 300 cycles at 200 mA g^{-1}, the capacity retention rate remains 91%.

In the above work, both air and chemical pre-oxidation are significant methods for preparing non-graphitized carbons using soft carbon precursors. However, the toxic gases generated during preparation and cost issues need to be carefully considered.

3 Electrochemical energy storage application of petroleum asphalt-based carbon materials

Petroleum asphalt-based carbon materials have great economic advantages and research value. At present, they have become promising electrode materials and have been widely used in electrochemical energy storage. The electrochemical energy storage performance of petroleum asphalt-based carbon materials is summarized in Table 1. The specific surface area characteristics and electrochemical energy storage performance of petroleum asphalt-based carbon materials obtained by different preparation strategies are compared in detail. It can be observed that the carbon materials prepared by alkaline activation favor multi-scale pores, while porous carbons prepared by air/chemical pre-oxidation and hard templates typically with lower specific surface area. Hence, the appropriate preparation method should be selected based on the requirements of the energy storage device for electrode materials.

3.1 Supercapacitors

Among the well-known various energy storage devices, carbon-based supercapacitors (SCs) renowned for high power density and long cycle stability, are a focal research area[75–76]. Currently, carbon materials are extensively explored as the elec-

Table 1 The electrochemical energy storage performance of petroleum asphalt-based carbon materials

Materials	Preparation strategy	S_{BET}/(m^2 g^{-1})	Device type	Capacity	Ref.
ZnMn$_2$O$_4$/PCF	ZnO template	98	Lithium-ion battery	760 mAh g^{-1} at 0.1 A g^{-1}	[24]
PCNS-2	KOH, NaOH activation	2053	Supercapacitor	169 F g^{-1} at 1 A g^{-1}	[31]
MnO$_2$/MnS$_2$/C-2	NaCl template, Heteroatom doping	–	Lithium-ion battery	827 mAh g^{-1} at 0.5 A g^{-1}	[32]
CPOP	Air pre-oxidation, high-temperature carbonization	–	Sodium-ion battery	300.6 mAh g^{-1} at 0.03 A g^{-1}	[33]
Pitch-C	Air pre-oxidation, high-temperature carbonization	–	Lithium-ion battery	332 mAh g^{-1} at 0.1 A g^{-1}	[35]
CNTs-PC	MgO template	1018	Supercapacitor	385.7 F g^{-1} at 1 A g^{-1}	[37]
HPCs	SiO$_2$ template, KOH activation	1953	Supercapacitor	341 F g^{-1} at 1 A g^{-1}	[38]
Fe$_3$O$_4$/PC	Fe$_2$O$_3$ template	–	Lithium-ion battery	785 mAh g^{-1} at 0.2 A g^{-1}	[42]
PACS	ZnO template	188	Lithium-ion battery	334 mAh g^{-1} at 1 A g^{-1}	[43]
CPC	MgO template, KOH activation	1512	Lithium-ion capacitor	120 mAh g^{-1} at 1 A g^{-1}	[45]
N,S-hPGNs	C$_3$N$_4$ template	1093	Supercapacitor	302 F g^{-1} at 1 A g^{-1}	[46]
MSC800	KCl/CaCl$_2$ molten salts	104	Lithium-ion battery	579 mAh g^{-1} at 2 A g^{-1}	[49]
MSC	NaCl/KCl molten salts	11	Lithium-ion battery	729 mAh g^{-1} at 0.1 A g^{-1}	[50]
HPCs	NaCl/KCl molten salts, KOH activation	2227	Supercapacitor	265 F g^{-1} at 0.05 A g^{-1}	[51]
HPCs	KCl molten salt, KOH activation	3581	Supercapacitor	277 F g^{-1} at 0.05 A g^{-1}	[58]
SHC	KOH activation	2231	Supercapacitor	315 F g^{-1} at 1 A g^{-1}	[60]
NTPCs	KHCO$_3$ activation	1229	Supercapacitor	80.32 F g^{-1} at 1 A g^{-1}	[61]
PHC	Air pre-oxidation, carbonization, Heteroatom doping	1	Sodium-ion battery	359.9 mAh g^{-1} at 0.015 A g^{-1}	[64]
HCPOP	Air pre-oxidation, high-temperature carbonization	7	Sodium-ion battery	312 mAh g^{-1} at 0.0186 A g^{-1}	[68]
HC	Air pre-oxidation, high-temperature carbonization	324	Sodium-ion battery	300.83 mAh g^{-1} at 0.02 A g^{-1}	[70]
HPPC	HNO$_3$ oxidation, high-temperature carbonization	1	Sodium-ion battery	226.8 mAh g^{-1} at 0.3 A g^{-1}	[73]
h-PC	Potassium citrate, g-C$_3$N$_4$ template, Heteroatom doping	996	Supercapacitor	437 F g^{-1} at 1 A g^{-1}	[81]
NPSC	NaCl template, Heteroatom doping	31	Sodium-ion battery	162 mAh g^{-1} at 1 A g^{-1}	[94]
NOC	Air pre-oxidation, high-temperature carbonization	177	Potassium-ion battery	347 mAh g^{-1} at 0.1 A g^{-1}	[101]

trode materials for SCs[77–78]. The energy storage mechanism of carbon-based electric double layer capacitors (EDLC) mainly depends on the reversible adsorption/desorption processes of electrolyte ions on the electrode surface. Therefore, petroleum asphalt can be modified through pore structure regulation and heteroatom doping to achieve rapid exchange of electrolyte ions and promote the rapid energy storage process.

Zhang et al.[79] obtained graphene-based activated carbon (G-ACs) by direct KOH chemical activation of petroleum asphalt, which has a high specific surface area (3 505 m^2/g) and surprising conductivity (32 S/m). Meanwhile, G-ACs exhibit superior rate performance and their cyclic voltammetry (CV) curves are similar to quasi-rectangles, indicating ideal capacitance performance (Fig. 7a). Pan et al.[58] guided the growth of 3D self-assembled carbon networks by KCl-assisted KOH activation of petroleum asphalt, preparing tightly interconnected porous carbon (HPC) (Fig. 7b). The HPC has an ultra-high specific surface area (3 581 m^2/g) and exposes abundant electrochem-

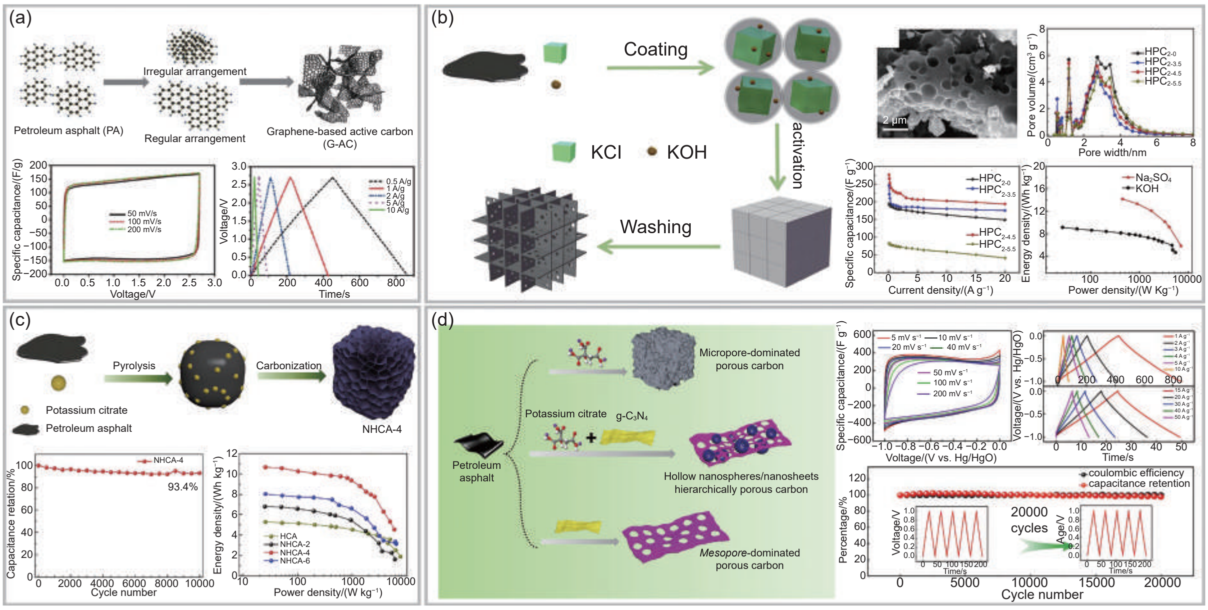

Fig. 7　(a) Schematic diagram for petroleum asphalt-based graphene-based active carbon (G-AC) and electrochemical performance for SCs[79]. (b)Schematic diagram for petroleum asphalt-based KOH activated carbonization hierarchical porous carbon (HPCs) and its morphology, pore size distribution, and electrochemical performance for SCs[58]. (c) Schematic diagram for layered porous carbon assembled from nanosheets of petroleum asphalt activated by potassium citrate and its electrochemical performance for SCs[80]. (d) Schematic diagram for heteroatom doped petroleum asphalt-based graded porous carbon (h-PC) with multi-scale structures of nanosheets/hollow nanospheres and electrochemical performance for SCs[81]. Reprinted with permission

ical active sites. Besides, HPC shows a high capacitance of 277 F g^{-1} at 0.05 A g^{-1} along with outstanding rate performance. When utilized in Na_2SO_4 electrolyte, HPC-based symmetric capacitor possesses a high specific energy density of 14.2 Wh kg^{-1} at a power density of 445 W kg^{-1}.

Furthermore, Guan et al.[80] utilized potassium citrate as a green activator to obtain nanosheet-assembled hierarchical carbon architecture using petroleum asphalt as the precursor (Fig. 7c). This method, which replaces traditional KOH, reduces environmental pollution and avoids the introduction of additional templates. The prepared porous carbon nanosheets promote effective electron/ion transfer channels, thus providing advantages in cycling stability and energy density. Yang et al.[81] adopted a simple dual template strategy to prepare heteroatom-doped petroleum asphalt-based graded porous carbon (h-PC) with multi-scale structures of nanosheets/hollow nanospheres (Fig. 7d). The h-PC, enriched with N, O, S heteroatoms and abundant ion-accessible surfaces, exhibits a high specific capacitance of 437 F g^{-1} at 1 A g^{-1}. Besides, the assembled symmetric SCs manifest robust cycling stability.

The above research works reflect the widespread application of petroleum asphalt-based porous carbon in energy storage SCs, offering cost-effective electrode materials. However, the field of SCs still faces challenges such as high material and maintenance costs, low charging/discharging efficiency, limited cycle life, and insufficient energy density. Future research should aim for exploring low-cost and environmental-friendly activation methods for the petroleum asphalt-based carbon materials for SCs.

3.2　Lithium-ion batteries

As a practical energy storage system, lithium-ion batteries (LIBs) are crucial for upgrading the automotive industry and effectively utilizing new energy[82–83]. However, for LIBs, the low capacity of graphite electrodes hinders their further development[84]. In addition, LIBs still cannot meet the market requirements in terms of charging rate and production cost. Thus, developing electrode materials with high energy density and stable cycling performance is essential for improving lithium-ion storage performance and addressing these problems. At present, the most frequently used anode materials for LIBs include metal compounds[85], transition metal alloys[86] and carbon materials[87], etc. Among them, carbon materials have become a research hotspot owing to their abundant sources, low cost, and stable structure. Petroleum asphalt, with high carbon yield and rich heteroatoms, can be converted into various structured carbon materials through simple oxidation and carbonization treatments, making it a highly potential anode material for LIBs. Gao et al.[65] synthesized electron-rich carbon nanosheets by mixing inexpensive supramolecular polymers of petroleum asphalt, melamine and phytic acid, followed by high-temperature carbonization (Fig. 8a). The interlayer spacing is expanded by co-

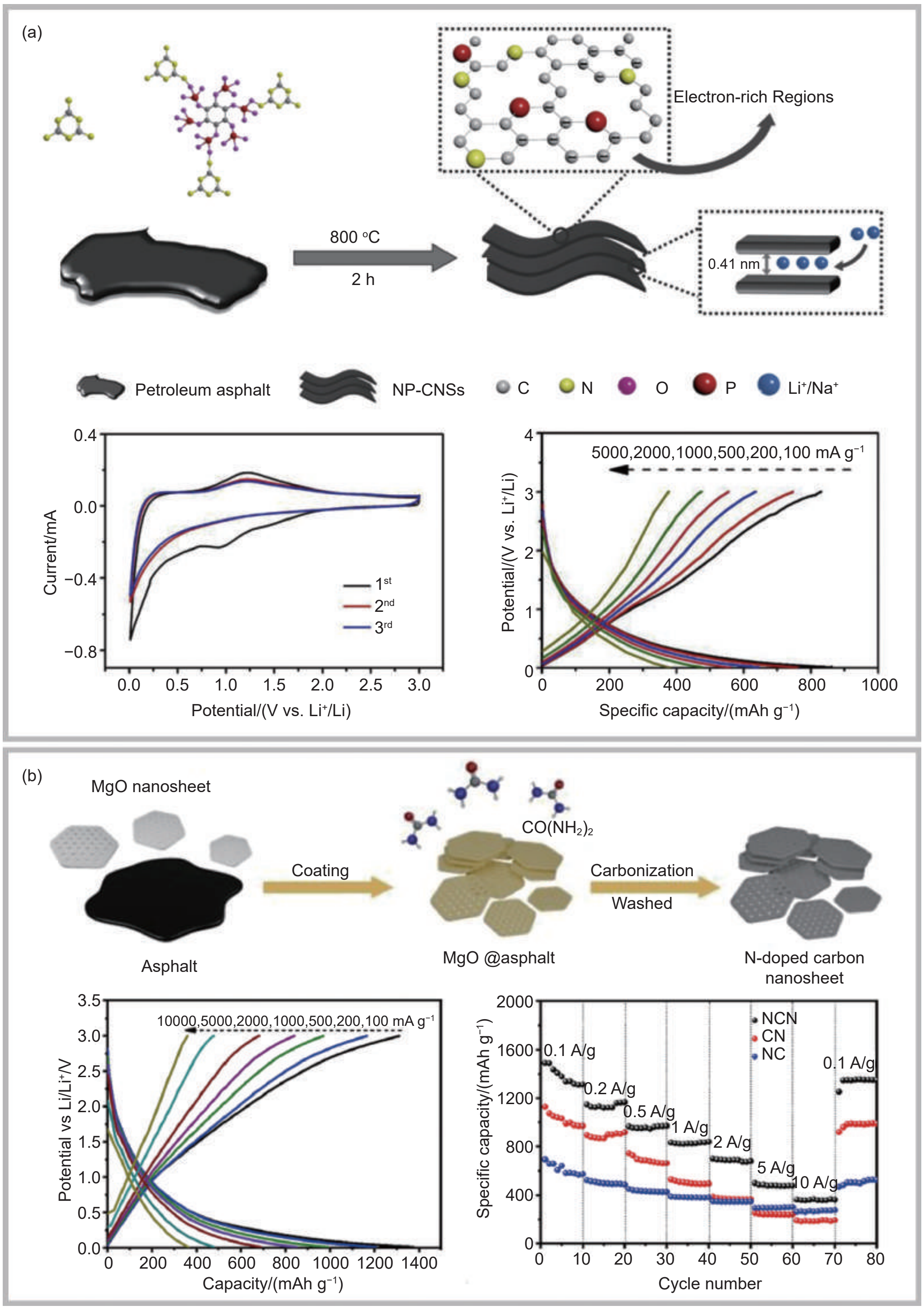

Fig. 8　(a) Schematic diagram for petroleum asphalt-based nitrogen and phosphorus co-doped carbon nanosheets (NP-CNSs) and electrochemical performance for LIBs[65]. (b) Schematic diagram for petroleum asphalt-based 2D nitrogen-doped carbon nanosheets (NCN) and electrochemical performance for LIBs[88]. Reprinted with permission doping with nitrogen (11.2%) and phosphorus (5.8%) heteroatoms. Specifically, melamine condenses into graphitic nitride at high temperatures, and then decomposes as a sacrificial template to form 2D carbon nanosheets in melted asphalt. Additionally, the blend of supramolecular polymers facilitates phosphorus doping and further nitrogen doping, ultimately inducing charge rearrangement and structural distortions within the graphene layers. Hence, the as-prepared electron-rich and expanded interlayer spacing carbon nanosheets (NP-CNSs) deliver extraordinary lithium-ion storage performance. The CV curves of NP-CNSs display characteristic of carbonaceous materials, exhibiting high Li^+ insertion/extraction reversibility. Meanwhile, NP-CNSs have good rate performance which sustain a stable capacity exceeding 379 mAh g^{-1} even at a high current density of 5 A g^{-1}.

Li et al.[88] fabricated N-doped 2D porous carbon nanosheets (NCN) from appealing porous MgO templates, petroleum asphalt, and urea (Fig. 8b). Urea, with high nitrogen content, provides abundant nitrogen doping, which can expand the interlayer distance of the carbon layer and improve electronic conductivity. After high-temperature carbonization, NCN generates a porous structure, providing a high specific surface area of 1 021 m^2 g^{-1}. Moreover, the 2D nanosheet structure promotes the intercalation and adsorption of Li^+. Benefiting from the high specific surface area and heteroatoms content, the as-prepared NCN shows a high capacity of 1 129 mAh g^{-1} at 0.1 A g^{-1} and a superb rate capability (580 mAh g^{-1} at 5 A g^{-1}). Nevertheless, LIBs still face limitations such as the scarcity of lithium resources and relatively low energy density. Therefore, further exploration is needed to investigate the impact of carbonization conditions, heteroatom doping types, and other factors on lithium-ion storage in petroleum asphalt-based carbon materials.

3.3 Sodium-ion batteries

In recent years, LIBs have been widely used in portable electronic devices and electric vehicles. However, with the expansion of the energy storage market and increasing daily consumption, lithium resources with limited reserves are insufficient to cater to future demands, particularly for grid-scale storage systems.

In the periodic table, sodium (Na) and lithium (Li) belong to the same main group and have similar chemical/electrochemical properties. Contrary to Li resources, Na resources are abundant[89–90]. Hence, SIBs are considered a promising candidate for secondary energy storage devices. Nevertheless, the larger ionic radius of Na^+ (1.02 Å vs. 0.76 Å of Li^+) and the higher standard electrochemical potential (−2.71 V Na/Na^+ and −3.04 V Li/Li^+ vs. SHE) make traditional graphite negative electrode materials no longer suitable for SIBs, resulting in limited energy density[91].

Dong et al.[92] compared the sodium storage performance of carbon materials prepared by direct pyrolysis of petroleum asphalt with those prepared by glucose pyrolysis carbon. It was found that asphalt pyrolysis carbon has a smaller specific surface area and interlayer spacing, as well as fewer oxygen-containing functional groups. As a consequence, the first Coulombic efficiency of asphalt pyrolysis carbon is significantly lower. This indicates that direct pyrolysis of petroleum asphalt is prone to form long-range ordered graphitic structures, which are not conducive to Na^+ storage.

To address the aforementioned issues, scientists have made efforts to produce high-performance carbon electrode materials by using petroleum asphalt as a carbon source. Guo et al.[67] prepared hard carbon materials based on petroleum asphalt through air pre-oxidation, and explored the effect of oxidation temperature on sample composition and microstructure. The results show that a large number of oxygen-containing functional groups are successfully introduced into the asphalt, inducing dehydrogenation condensation and oxidative crosslinking. The final obtained amorphous carbon has a high charging specific capacity of 276.8 mAh g^{-1} at 100 mA g^{-1} and a high ICE of 73.38%. Similarly, Qiu et al.[93] used petroleum asphalt and phenolic resin as precursors, with NaCl template to widen interlayer spacing in 3D porous hard soft composite carbon (3DHSC) for enhanced sodium storage (Fig. 9a). The results indicate that sodium chloride templates are beneficial for constructing rich

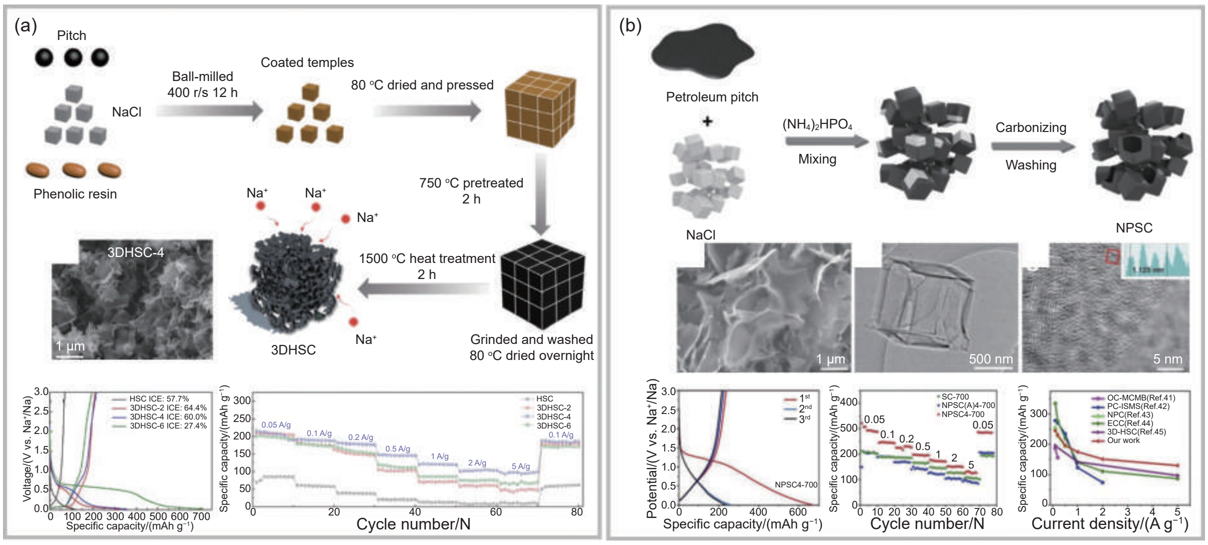

Fig. 9 (a) Schematic diagram for 3D porous soft hard composite carbon (3DHSC) carbonized by mixing petroleum asphalt and phenolic resin for SIBs[93]. (b) Schematic diagram for petroleum asphalt-based carbon materials doped with N and P heteroatoms by high-temperature pyrolysis carbonization and electrochemical performance for SIBs[94]. Reprinted with permission

mesoporous and macroporous structures, promoting sodium ion diffusion. Typically, the optimized carbon material exhibits high reversible capacity (215 mAh g^{-1} at 0.05 A g^{-1}), good rate capability (97 mAh g^{-1} at 5 A g^{-1}), and high ICE (60%). This work demonstrates the significant advantages of salt templates in constructing asphalt-based carbon materials and has great application prospects.

Zhao et al.[94] prepared petroleum asphalt-based carbon materials doped with N and P heteroatoms through high-temperature pyrolysis carbonization (NPSC) (Fig. 9b). NPSC has a nanobox-shaped morphology and consists of amorphous carbon domains with large interlayer spacing. The nanobox structure and defects induced by NaCl are conducive to the transport of Na^+. Although the optimized material has a lower initial efficiency, it exhibits superior rate performance (162 mAh g^{-1} at 1 A g^{-1} to 130 mAh g^{-1} at 5 A g^{-1}), achieving a high specific capacity, surpassing many currently reported SIBs anode materials.

The aforementioned studies employed salt templates and heteroatom doping to develop promising sodium negative electrodes. However, Na^+ storage devices still confront challenges like low charging/discharging rates, poor safety, and high production costs[95]. Therefore, focusing on efficient template removal and precise heteroatom doping is imperative for cost-effective, long-lasting asphalt-derived carbon negative electrodes for SIBs.

3.4 Potassium-ion batteries

Potassium ion batteries (KIBs) are also considered an ideal alternative to LIBs, with their abundant potassium resources, low cost, and high output voltage[96–97]. However, the large radius of potassium ions leads to slow kinetics and severe volume expansion during charging and discharging, which restricts the development of traditional electrode materials[98]. The disordered structure of hard carbon can accommodate the large volume changes caused by the insertion of K ions with larger radii while maintaining structural integrity[99–100]. Consequently, hard carbon also exhibits good potassium-ion storage potential. Currently, the use of petroleum asphalt-derived hard carbon has been widely applied in the research of KIBs negative electrode materials. For instance, Sun et al.[101] suppressed the graphitization of asphalt during high-temperature pyrolysis through pre-oxidation, inducing the formation of a turbulent layer structure of hard carbon, which is beneficial for structural stability. This strategy also introduces nitrogen and oxygen functional groups into asphalt, enhancing the potassium storage capacity of carbon materials. Yin et al.[102] prepared hard carbon materials for both LIBs and KIBs by co-carbonizing phenolic resin with asphalt.

The optimized material provided a great potassium reversible capacity (321.9 mAh g^{-1}). The above work reflects the potential application of asphalt-based carbon materials in KIBs. However, KIBs still face significant volume changes during potassium ion insertion/deintercalation, severe side reactions, and capacity degradation challenges caused by potassium dendrite growth. In the future, more efforts should focus on developing materials that address these issues and enhance performance across a range of applications.

4 Conclusions and prospects

Based on the above research progress, and supported by national policies and the expanding energy storage market, significant progresses have been made in the field of energy storage in recent years, despite the practical issues faced by petroleum asphalt precursors in the process of being converted into high-capacity energy storage carbon electrode materials. Notably, various preparation methods have distinct characteristics, emphasizing the need for developing advanced strategies capable of meeting the increasing demand of energy storage scenarios.

In this review, we initially summarized various typical preparation methods for high-performance electrochemical energy storage materials using petroleum asphalt as a carbon source, as well as their applications in various representative energy storage devices. This provides some references for the high value-added utilization of petroleum asphalt-based carbon sources. To further promote the industrial application of petroleum asphalt-based precursors in electrochemical energy storage, research can be carried out in the following aspects in the future:

(1) The composition and structure of petroleum asphalt obtained from different origins and process routes are complex, characterized by varying ash content, and the inherent thermoplastic properties of asphalt make it susceptible to clumping during carbonization. Future research should focus on revealing the precise control of complex compositions in petroleum asphalt raw materials and their impact on the morphology and properties of carbon materials prepared.

(2) Although high-performance asphalt-based porous carbon materials can be prepared using strategies assisted by other reagents such as template method or molten salt method, the treatment of template agent and molten salt is also a challenge. Addressing this issue holds significance for expanding energy storage applications while also preserving the environment.

(3) The use of an alkali activator to modify thermoplastic asphalt can construct hierarchical pore structures during the melting process, but production costs and subsequent alkali activator treatment issues still need to be considered.

(4) Further exploration is needed to achieve precise control of heteroatom doping in petroleum asphalt through strategies such as pre-oxidation. Not all heteroatoms are suitable for improving the energy storage performance of carbon materials. Therefore, considering the properties of asphalt combined with a heteroatom-doping strategy is favorable for stimulating energy storage potential.

(5) The application scope of different forms of petroleum asphalt-based carbon materials in the field of electrochemical energy storage is increasingly expanding. However, efficient methods to convert petroleum asphalt into high value-added products are still lacking. Efforts should be made to use advanced characterization methods to reveal the energy storage mechanism of carbon materials and prepare advanced carbon materials to meet the demand for high energy density.

In summary, this article reviews the latest research progress of petroleum asphalt-based carbon materials in the field of energy storage. Although there remains a long way to go before achieving environmentally friendly and high value-added practical applications of petroleum asphalt materials, we believe that this review can offer valuable insights and guidance for the design of future top-tier energy storage materials.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

We gratefully acknowledge the financial supports from the National Natural Science Foundation of China (22238012 and 22178384), and Science Foundation of China University of Petroleum, Beijing (2462024QNXZ003).

References

[1] Wang H L, Dai H J. Strongly coupled inorganic-nano-carbon hybrid materials for energy storage[J]. Chemical Society Reviews, 2013, 42(7): 3088-3113.

[2] Su D S, Centi G. A perspective on carbon materials for future energy application[J]. Journal of Energy Chemistry, 2013, 22(2): 151-173.

[3] Kostoglou N, Koczwara C, Prehal C, et al. Nanoporous activated carbon cloth as a versatile material for hydrogen adsorption, selective gas separation and electrochemical energy storage[J]. Nano Energy, 2017, 40: 49-64.

[4] Larcher D, Tarascon J M. Towards greener and more sustainable batteries for electrical energy storage[J]. Nature Chemistry, 2015, 7(1): 19-29.

[5] Zhang C, Lv W, Tao Y, et al. Towards superior volumetric performance: design and preparation of novel carbon materials for energy storage[J]. Energy & Environmental Science, 2015, 8(5): 1390-1403.

[6] Xiao J, Han J W, Zhang C, et al. Dimensionality, function and performance of carbon materials in energy storage devices[J]. Advanced Energy Materials, 2021, 12(4): 2100775.

[7] Zhong M Z, Zhang M, Li X F. Carbon nanomaterials and their composites for supercapacitors[J]. Carbon Energy, 2022, 4(5): 950-985.

[8] Xue B C, Xu J H, Xiao R. Synthesis of hierarchically porous carbon with tailored porosity and electrical conductivity derived from hard-soft carbon precursors for enhanced capacitive performance[J]. ACS Sustainable Chemistry & Engineering, 2021, 9(47): 15925-15934.

[9] Zhang G L, Guan T T, Wang N, et al. Small mesopore engineering of pitch-based porous carbons toward enhanced supercapacitor performance[J]. Chemical Engineering Journal, 2020, 399: 125818.

[10] Ning H, Wang L H, He S B, et al. Research process of petroleum pitch-based carbon materials in electrochemical applications[J]. Petroleum Processing and Petrochemicals, 2021, 52(10): 38-45.

[11] Xu X C, Zhou X Z, Wei M, et al. Automatic analyzer for determining four components of petroleum asphalt[J]. Shandong Chemical Industry, 2024, 53(7): 153-155.

[12] Li X C. Discussion on method to determine four components in asphalt[J]. China Building Waterproofing, 2019, 2: 52-55.

[13] Zhang R, Ji J, You Z P, et al. Modification mechanism of using waste wood-based bio-oil to modify petroleum asphalt[J]. Journal of Materials in Civil Engineering, 2020, 32(12): 04020375.

[14] Dong Y W, Xing G Z, Jin L E, et al. Co-carbonization of brominated petroleum pitch, coal tar pitch and benzoyl chloride to prepare cokes[J]. New Carbon Materials, 2019, 34(3): 258-266.

[15] Liu J Y, Liu Y, Li P, et al. Fe-N-doped porous carbon from petroleum asphalt for highly efficient oxygen reduction reaction[J]. Carbon, 2018, 126: 1-8.

[16] Cheng Z N, Wang Y, Jin D K, et al. Petroleum pitch-derived porous carbon as a metal-free catalyst for direct propane dehydrogenation to propylene[J]. Catalysis Today, 2023, 410: 164-174.

[17] He F X, Chen X, Zang N, et al. Overview of properties and applications of petroleum bitumen[J]. Carbon Techniques, 2022, 3: 42-46.

[18] Jiang M C, Sun N, Ali Soomro R, et al. The recent progress of pitch-based carbon anodes in sodium-ion batteries[J]. Journal of Energy Chemistry, 2021, 55: 34-47.

[19] Yang Y K, Li Z G, Zhao J S, et al. Structural engineering of pitch-based porous carbon and its application in supercapacitors: A review[J]. Journal of Energy Storage, 2023, 74: 109334.

[20] Ji L C, Zhao Y, Cao L J, et al. A fundamental understanding of structure evolution in the synthesis of hard carbon from coal tar pitch for high-performance sodium storage[J]. Journal of Materials Chemistry A, 2023, 11(48): 26727-26741.

[21] Fan M. Influence of preparation methods on the properties of petroleum pitch-based porous carbon materials[J]. Petrochemical Industry Application, 2022, 41(5): 102-107.

[22] Xiao N, Qiu J S. Progress in synthesis and applications of functional carbon materials from coal tar pitch[J]. Chemical Industry and Engineering Progress, 2016, 35(6): 1804-1811.

[23] Zhao Q S, Xie H, Ning H, et al. Intercalating petroleum asphalt into electrospun ZnO/Carbon nanofibers as enhanced free-standing anode for lithium-ion batteries[J]. Journal of Alloys and Compounds, 2018, 737: 330-336.

[24] Li P, Liu J Y, Liu Y, et al. Three-dimensional $ZnMn_2O_4$/porous carbon framework from petroleum asphalt for high performance lithium-ion battery[J]. Electrochimica Acta, 2015, 180: 164-172.

[25] Wang Y F, Zhang L, Hou H Q, et al. Recent progress in carbon-based materials for supercapacitor electrodes: a review[J]. Journal of Materials Science, 2020, 56(1): 173-200.

[26] Zhai Y P, Dou Y Q, Zhao D Y, et al. Carbon materials for chemical capacitive energy storage[J]. Advanced Materials, 2011, 23(42): 4828-4850.

[27] Yuksel R, Karakehya N. High energy density biomass-derived activated carbon materials for sustainable energy storage[J]. Carbon, 2024, 221: 118934.

[28] Díez N, Fuertes A B, Sevilla M. Molten salt strategies towards carbon materials for energy storage and conversion[J]. Energy Storage Materials, 2021, 38: 50-69.

[29] Ni J F, Li Y. Carbon nanomaterials in different dimensions for electrochemical energy storage[J]. Advanced Energy Materials,

2016, 6(17): 1600278.

[30] Wang Z T, Zhang M Q, Ma W T, et al. Application of carbon materials in aqueous zinc ion energy storage devices[J]. Small, 2021, 17(19): e2100219.

[31] Wang D W, Xu L, Nai J W, et al. A versatile Co-Activation strategy towards porous carbon nanosheets for high performance ionic liquid based supercapacitor applications[J]. Journal of Alloys and Compounds, 2019, 786: 109-117.

[32] Li Y, Yang W, Tu Z Q, et al. In-situ bonding with sulfur in petroleum asphalt to synthesize transition metal (Mn, Mo, Fe, or Co)-based/carbon composites for superior lithium storage[J]. Carbon, 2021, 182: 700-710.

[33] Lu Y X, Zhao C L, Qi X G, et al. Pre-oxidation-tuned microstructures of carbon anodes derived from pitch for enhancing Na storage performance[J]. Advanced Energy Materials, 2018, 8(27): 1800108.

[34] Dou X W, Hasa I, Saurel D, et al. Hard carbons for sodium-ion batteries: Structure, analysis, sustainability, and electrochemistry[J]. Materials Today, 2019, 23: 87-104.

[35] Ge Z, Chen X, Zhang X G, et al. Porous MnO/pitch carbon composite as an anode material for low-cost and high-performance lithium-ion battery[J]. Chemical Engineering Science, 2024, 285: 119625.

[36] Li Y M, Mu L Q, Hu Y S, et al. Pitch-derived amorphous carbon as high performance anode for sodium-ion batteries[J]. Energy Storage Materials, 2016, 2: 139-145.

[37] Song X Y, Jiang R Y, Zhang L. In-situ growth of CNTs-porous carbon from asphalt with superior double-layer capacitive performance[J]. Applied Surface Science, 2022, 583: 152549.

[38] Abudu P, Wang L X, Xu M J, et al. Hierarchical porous carbon materials derived from petroleum pitch for high-performance supercapacitors[J]. Chemical Physics Letters, 2018, 702: 1-7.

[39] Xie M M, Li D Q, He X, et al. Nitrogen-doped meso-macroporous carbon from waste asphalt as high-performance anode materials for alkali-ion batteries[J]. Sustainable Materials and Technologies, 2023, 35: e00535.

[40] Cao B, Liu H, Xu B, et al. Mesoporous soft carbon as an anode material for sodium ion batteries with superior rate and cycling performance[J]. Journal of Materials Chemistry A, 2016, 4(17): 6472-6478.

[41] Jiang Y C, He Z F, Du Y Y, et al. In-situ ZnO template preparation of coal tar pitch-based porous carbon-sheet microsphere for supercapacitor[J]. J Colloid Interface Sci, 2021, 602: 721-731.

[42] Liu Y, Li P, Wang Y W, et al. A green and template recyclable approach to prepare Fe_3O_4/porous carbon from petroleum asphalt for lithium-ion batteries[J]. Journal of Alloys and Compounds, 2017, 695: 2612-2618.

[43] Li P, Liu J Y, Wang Y W, et al. Synthesis of ultrathin hollow carbon shell from petroleum asphalt for high-performance anode material in lithium-ion batteries[J]. Chemical Engineering Journal, 2016, 286: 632-639.

[44] Qi Y H, Fan W Y, Nan G Z. Free-standing, binder-free polyacrylonitrile/asphalt derived porous carbon fiber-a high capacity anode material for sodium-ion batteries[J]. Materials Letters, 2017, 189: 206-209.

[45] Lin R D, Gao F, Zhang X L, et al. N-doped graphene nanolayer originated from the one-step template-induction methodology as anode for high-performance Li-ion capacitor[J]. Carbon, 2022, 200: 84-93.

[46] Yang W, Deng B J, Hou L Q, et al. N, S co-doped hierarchical porous graphene nanosheets derived from petroleum asphalt via in situ texturing strategy for high-performance supercapacitors[J]. Industrial & Engineering Chemistry Research, 2019, 58(11): 4487-4494.

[47] Zeng K, Yang X Y, Xie Y P, et al. Molten salt pyrolysis of biomass: The evaluation of molten salt[J]. Fuel, 2021, 302: 121103.

[48] Song Y L, Wang Z C, Yan Y D, et al. Molten salt synthesis and supercapacitor properties of oxygen-vacancy $LaMnO_{3-\delta}$[J]. Journal of Energy Chemistry, 2020, 43: 173-181.

[49] Wang Y X, Tian W, Wang L H, et al. A tunable molten-salt route for scalable synthesis of ultrathin amorphous carbon nanosheets as high-performance anode materials for lithium-ion batteries[J]. ACS Applied Materials & Interfaces, 2018, 10(6): 5577-5585.

[50] Wang Y X, Wang Y W, Liu J L, et al. Preparation of carbon nanosheets from petroleum asphalt via recyclable molten-salt method for superior lithium and sodium storage[J]. Carbon, 2017, 122: 344-351.

[51] Pan L, Li X X, Wang Y X, et al. 3D interconnected honeycomb-like and high rate performance porous carbons from petroleum asphalt for supercapacitors[J]. Applied Surface Science, 2018, 444: 739-746.

[52] Sevilla M, B. Fuertes A. Direct synthesis of highly porous interconnected carbon nanosheets and their application as high-performance supercapacitors[J]. ACS Nano, 2014, 8(5): 5069-5078.

[53] Nabais J M V, Nunes P, Carrott P J M, et al. Production of activated carbons from coffee endocarp by CO_2 and steam activation[J]. Fuel Processing Technology, 2008, 89(3): 262-268.

[54] Yi H, Nakabayashi K J, Yoon S H, et al. Pressurized physical activation: a simple production method for activated carbon with a highly developed pore structure[J]. Carbon, 2021, 183: 735-742.

[55] Ding Y X, Qi J, Hou R L, et al. Preparation of high-performance hierarchical porous activated carbon via a multistep physical activation method for supercapacitors[J]. Energy & Fuels, 2022, 36(10): 5456-5464.

[56] Guo M C, Liu S L, He F X, et al. Electrochemical properties of coal pitch-based three-dimensional porous carbon as electrode materials for supercapacitors[J]. Journal of Fuel Chemistry and Technology, 2021, 49(11): 1648-1655.

[57] Zou Y L, Wang H F, Xu L F, et al. Synergistic effect of CO_2 and H_2O co-activation of Zhundong coal at a low burn-off rate on high performance supercapacitor[J]. Journal of Power Sources, 2023, 556: 232509.

[58] Pan L, Wang Y X, Hu H, et al. 3D self-assembly synthesis of

hierarchical porous carbon from petroleum asphalt for supercapacitors[J]. Carbon, 2018, 134: 345-353.

[59] Li C, Yan L J, Lv M L, et al. Spongy porous carbon nanosheets obtained by one-step oxidation-activation of asphalt with KHC_2O_4 activator: Application in the cathode of zinc storage devices[J]. Science of the Total Environment, 2024, 909: 168519.

[60] Xie Y Y, Yu C, Guo W, et al. A long/short-range interconnected carbon with well-defined mesopore for high-energy-density supercapacitors[J]. Nano Research, 2021, 15(2): 1399-1408.

[61] Zhang Y, Fang H Q, Guan L, et al. Effect of asphalt component distribution characteristics in layered porous carbon on performance of supercapacitors[J]. Journal of Power Sources, 2024, 593: 233966.

[62] Li T, Huang X, Lei S, et al. Two-dimensional nitrogen and phosphorus co-doped mesoporous carbon-graphene nanosheets anode for high-performance potassium-ion capacitor[J]. Energy Materials, 2023, 3: 300018.

[63] Shaker M, Ghazvini A A S, Shahalizade T, et al. A review of nitrogen-doped carbon materials for lithium-ion battery anodes[J]. New Carbon Materials, 2023, 38(2): 247-278.

[64] Wang H, Liu S T, Lei C, et al. P-doped hard carbon material for anode of sodium ion battery was prepared by using polyphosphoric acid modified petroleum asphalt as precursor[J]. Electrochimica Acta, 2024, 477: 143812.

[65] Gao C, Feng J Z, Dai J R, et al. Manipulation of interlayer spacing and surface charge of carbon nanosheets for robust lithium/sodium storage[J]. Carbon, 2019, 153: 372-380.

[66] Miao Y L, Zong J, Liu X J. Phosphorus-doped pitch-derived soft carbon as an anode material for sodium ion batteries[J]. Materials Letters, 2017, 188: 355-358.

[67] Guo H Y, Li Y Y, Wang C L, et al. Effect of the air oxidation stabilization of pitch on the microstructure and sodium storage of hard carbons[J]. New Carbon Materials, 2021, 36(6): 1073-1078.

[68] Daher N, Huo D, Davoisne C, et al. Impact of preoxidation treatments on performances of pitch-based hard carbons for sodium-ion batteries[J]. ACS Applied Energy Materials, 2020, 3(7): 6501-6510.

[69] Liu M Q, Wang Y H, Wu F, et al. Advances in carbon materials for sodium and potassium storage[J]. Advanced Functional Materials, 2022, 32(31): 2203117.

[70] Xu R, Yi Z L, Song M X, et al. Boosting sodium storage performance of hard carbons by regulating oxygen functionalities of the cross-linked asphalt precursor[J]. Carbon, 2023, 206: 94-104.

[71] Yang Y K, Wang J S, Zuo P P, et al. Layer-stacked graphite-like porous carbon for flexible all-solid-state supercapacitor[J]. Chemical Engineering Journal, 2021, 425: 130609.

[72] Wang Y L, Chen X H, Ding M J, et al. Oxidation of coal pitch by H_2O_2 under mild conditions[J]. Energy & Fuels, 2018, 32(1): 796-800.

[73] Xiong Z Y, Yue L, Zhang Y, et al. Structural regulation of asphalt-based hard carbon microcrystals based on liquid-phase crosslinking to enhance sodium storage[J]. Journal of Colloid And Interface Science, 2024, 658: 610-616.

[74] Wang J, Yan L, Liu B H, et al. A solvothermal pre-oxidation strategy converting pitch from soft carbon to hard carbon for enhanced sodium storage[J]. Chinese Chemical Letters, 2023, 34(4): 107526.

[75] Liu Z D, Duan C P, Dou S M, et al. Ultrafast porous carbon activation promises high-energy density supercapacitors[J]. Small, 2022, 18(23): e2200954.

[76] Dong Y, Zhu J Y, Li Q Q, et al. Carbon materials for high mass-loading supercapacitors: filling the gap between new materials and practical applications[J]. Journal of Materials Chemistry A, 2020, 8(42): 21930-21946.

[77] Shao Y L, El-Kady M F, Sun J Y, et al. Design and mechanisms of asymmetric supercapacitors[J]. Chemical Reviews, 2018, 118(18): 9233-9280.

[78] Xie P, Yuan W, Liu X B, et al. Advanced carbon nanomaterials for state-of-the-art flexible supercapacitors[J]. Energy Storage Materials, 2021, 36: 56-76.

[79] Wang B, Xie P Y, Zhang M, et al. Preparation of graphene-based active carbons from petroleum asphalt for high-performance supercapacitors without added conducting materials[J]. Science China Technological Sciences, 2022, 65(12): 2866-2873.

[80] Guan L, Pan L, Peng T Y, et al. Green and scalable synthesis of porous carbon nanosheet-assembled hierarchical architectures for robust capacitive energy harvesting[J]. Carbon, 2019, 152: 537-544.

[81] Yang W, Wang P, Tu Z Q, et al. Heteroatoms-doped hierarchical porous carbon with multi-scale structure derived from petroleum asphalt for high-performance supercapacitors[J]. Carbon, 2022, 187: 338-348.

[82] Liu H, Liu X X, Li W, et al. Porous carbon composites for next generation rechargeable lithium batteries[J]. Advanced Energy Materials, 2017, 7(24): 1700283.

[83] Zhang Y, Wang J R, Xue Z G. Electrode protection and electrolyte optimization via surface modification strategy for high-performance lithium batteries[J]. Advanced Functional Materials, 2023, 34: 2311925.

[84] Guo J Z, Yang Y, Liu D S, et al. A practicable Li/Na-ion hybrid full battery assembled by a high-voltage cathode and commercial graphite anode: superior energy storage performance and working mechanism[J]. Advanced Energy Materials, 2018, 8(10): 1702504.

[85] Tang S A, Guo W, Fu Y Z. Advances in composite polymer electrolytes for lithium batteries and beyond[J]. Advanced Energy Materials, 2020, 11(2): 2000802.

[86] Clément R J, Lun Z, Ceder G. Cation-disordered rocksalt transition metal oxides and oxyfluorides for high energy lithium-ion cathodes[J]. Energy & Environmental Science, 2020, 13(2): 345-373.

[87] Wu H Y, Wei L, Li W, et al. Highly conductive carbon/carbon composites as advanced multifunctional anode materials for structural lithium-ion batteries[J]. Advanced Functional Materials, 2024, 2403729.

[88] Li S L, Liu P F, Zheng X, et al. High-performance dual carbon lithium-ion capacitors based on nitrogen-doped 2D carbon nanosheets as both anode and cathode[J]. Electrochimica Acta, 2022, 428: 140921.

[89] Liu H C, Zhu S, Chang Y Z, et al. Pitch-based carbon materials: a review of their structural design, preparation and applications in energy storage[J]. New Carbon Materials, 2023, 38(3): 459-473.

[90] Huang S, Qiu X Q, Wang C W, et al. Biomass-derived carbon anodes for sodium-ion batteries[J]. New Carbon Materials, 2023, 38(1): 40-66.

[91] Wu X, Sun B, Liu Y D, et al. Research progress in preparation technology of pitch-based carbon anode materials for sodium ion batteries[J]. CIESC Journal, 2024, 75(4): 1270-1283.

[92] Dong W, Yang S B, Shen D, et al. Performance of pitch and glucose pyrocarbons for reversible sodium storage[J]. New Carbon Materials, 2017, 32(3): 227-233.

[93] Qiu D, Cao T F, Zhang J, et al. Precise carbon structure control by salt template for high performance sodium-ion storage[J]. Journal of Energy Chemistry, 2019, 31: 101-106.

[94] Zhao Y, Cong Y, Ning H, et al. N, P co-doped pitch derived soft carbon nanoboxes as high-performance anodes for sodium-ion batteries[J]. Journal of Alloys and Compounds, 2022, 918: 165691.

[95] Liu Q Y, Chen J C, Du D N, et al. Electrochemically prelithiated carbon anodes with regulated Na-ion intercalation behaviours for advanced sodium-ioni energy storage devices[J]. Journal of Materials Chemistry A, 2023, 11(33): 17491-17502.

[96] Pramudita J C, Sehrawat D, Goonetilleke D, et al. An initial review of the status of electrode materials for potassium-ion batteries[J]. Advanced Energy Materials, 2017, 7(24): 1602911.

[97] Li L, Liu L J, Hu Z, et al. Understanding high-rate K^+-solvent co-intercalation in natural graphite for potassium-ion batteries[J]. Angewandte Chemie International Edition, 2020, 59(31): 12917-12924.

[98] Shao M J, Li C X, Li T, et al. Pushing the energy output and cycling lifespan of potassium-ion capacitor to high level through metal-organic framework derived porous carbon microsheets anode[J]. Advanced Functional Materials, 2020, 30(51): 2006561.

[99] Wu X, Chen Y L, Xing Z, et al. Advanced carbon-based anodes for potassium-ion batteries[J]. Advanced Energy Materials, 2019, 9(21): 1900343.

[100] Li T, Zhao H, Li C X, et al. Recent progress and prospects in anode materials for potassium-ion capacitors[J]. New Carbon Materials, 2021, 36(2): 253-277.

[101] Sun Q, Li D P, Cheng J, et al. Nitrogen-doped carbon derived from pre-oxidized pitch for surface dominated potassium-ion storage[J]. Carbon, 2019, 155: 601-610.

[102] Yin X P, Zhao Y F, Wang X, et al. Modulating the graphitic domains of hard carbons derived from mixed pitch and resin to achieve high rate and stable sodium storage[J]. Small, 2022, 18(5): e2105568.