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Template-free synthesis of hierarchical mesoporous carbon: Based on functional coal tar pitches with carboxylation and diketone structures

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An efficient and easy template-free method for the preparation of hierarchical porous carbons (HPCs) has been developed using low-priced coal tar pitch (CP) as the starting material. Application of the diketone (-COCO-) radical provides a carbonyl methylene group for polycyclic aromatic hydrocarbons by condensation and produces an effective micro-mesoporous network with a high specific surface area. With the help of controlled Friedel-Crafts reaction and oxidation, carboxyl-functionalized CP is obtained as the stratified porous CP precursor, and the high-temperature decarboxylation (>230°C) helped in generating well-developed micro-mesoporous carbon. The total pore volume of porous carbon of 1277.3 and 1.45 cm^{3}g^{-1} the maximum BET surface area suggests that the rapid electrolyte ion exchange and charge transportability would be better for the electrochemical capacitor.

Keywords: Carboxylation, Coal tar pitches, Electrochemical properties, Hierarchical porous carbons

Porous carbon materials are the core of many technological applications, such as electrochemical energy storage and gas separation, purification. Among them, the controlled porous carbon is a commonly used electrode material for commercially available supercapacitors due to its large surface area, adjustable pore size, and acceptable cost[1,2]. In addition to its high conductivity and large surface area, the ideal carbon material should also display a hierarchical porous texture that joined mesopores, macropores, and micropores[3,4]. It has been suggested that macropores would serve as ion-buffering reservoirs inside carbon materials, while mesopores would provide channels for fast ion transport; furthermore, micropores offer locations for charge accommodation[5,6]. For these reasons, a sustainable method for the preparation of highly porous carbons has drawn significant research interest, and it remains a challenge to be overcome[7,8]. Recently, several approaches have been proposed to synthesize hierarchical porous carbons, such as the activation process, the template method, polymer blend carbonization, and organic aerogelcarbonization[9,10]. However, these studies did not provide a clear picture of the overall scope of the process of activation mechanism responsible for the generation of porosity.

Template strategies have been used to prepare porous carbons by using either a hard or soft template[11,12]. Various inorganic materials such as silica nanoparticles, mesoporous silica materials, zeolites, anodic alumina membranes, and metal-organic frameworks have been successfully used as hard templates. However, many limitations such as the sacrificial use and difficulties of synthesis of various templates additions, or the removal process that would usually increase processing complexity and the costs[13,14]. A feasible synthesis method for preparing porous carbon materials should be effectively regulated with a controlled pore network and offer convenient application.

Coal tar pitch (CP) is a by-product of the cooking process in the coal industry and is often used as carbonaceous precursors for carbon materials due to its rich sources, high carbon output, and good cost-efficiency. Since it contains a large number of aromatic heterocyclic compounds, the pitch would create carbons with different characteristic properties and structures. The Friedel-Crafts reaction would be the main strategy to produce extremely porous hyper-cross-linked materials[15]. CP contains hundreds of poly-aromatic molecules with different molecular sizes and varied chemical structures. When CP is charred for the synthesis of porous carbon materials, it is difficult to propose a clear point on every single component and its fine structure, and an ordering process would be necessary for the carbonation of CP[16].

In this paper, an effective template-free method has been successfully developed to prepare hierarchical porous carbons (HPCs) in which low-cost CP is used as a carbonaceous precursor. As shown in Scheme 1, a controllable Friedel-Crafts reaction of CP via introducing diketone. A diketone (-COCO-) bridge between polycyclic aromatic hydrocarbons would increase the crossing density and would confer a high level of controllability during the charring process. This study investigated the C-C cleavage of diketones for its carbonyl methylene condensation, and also the subsequent carboxyl-functionalized tar pitch with decarboxylation during the elastic-plastic side formation phase.

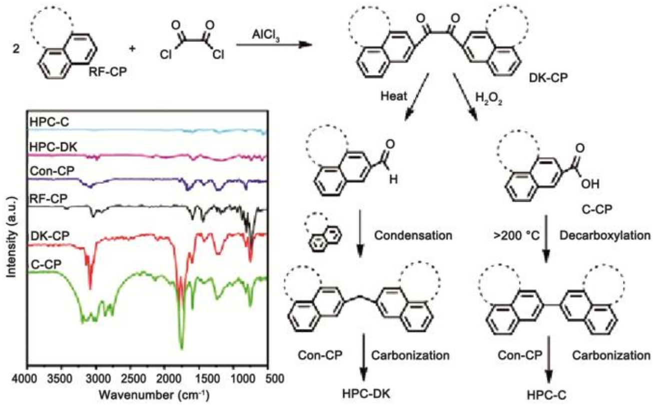
Materials and Methods

Materials

Raw CP was produced by the Anshan Iron and Steel Group Co. Ltd. (Anshan, China). A refined coal tar pitch (RF-CP) with a softening point of 33°C was gotten by a blended solvent-extraction strategy and its compositions. The most properties of the RFCP and DKCP have appeared in Table 1. Anhydrous aluminum chloride ($AlCl_3$) was from Tianjin Guangfu Fine Chemical Reagent Co. Ltd. (Tianjin, China). Oxalyl chloride (OC), hydrochloric corrosive (HCl), hydrogen peroxide (H_2O_2), and dichloroethane (DCE) were secured from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); and all chemical reagents were of analytical grade.

Synthesis of DK-CP and carboxylic

To produce carbonyl-functional CP, a refined coal tar pitch (RF-CP) was obtained with a softening point of 33°C. Oxalyl chloride (OC) was used as an external cross-linker. As shown in Scheme 1, first 50 g RF-CP was dissolved in 500 mL dichloromethane and then a 50 g $AlCl_3$ solution with oxalyl chloride was added dropwise under argon atmosphere. The resulting mixture was stirred for 6 h at 40°C and the reaction was ended by adding ethanol solution. After filtering and washing with ethanol solution and hydrochloric acid, the product was subjected to heat drying. To study the effects of polymerization, different combinations of coal tar pitch (DK-CP) with OC referred to as DK-CP-1,-2,-3 respectively, in 0.3, 0.6, and 0.9 weight ratios and the obtained diketone-functionalized DK-CP-3 were decomposed to carboxylic CP (C-CP) with H_2O_2 at 40°C. Under the N_2 atmosphere, the dark brown carbonized samples were heated in a tube furnace. Carbonation was finished within 2 h with a heating rate of 2 °C min^{-1}, up to 800°C.



Scheme 1 — Structural variation of RF-CP reacting with OC during the carbonization process

Table 1 — Compositions of refined coal tar pitch and raw coal tar pitch

Name	α fractions (%)	β fractions (%)	γ fractions (%)	Softening point (°C)	QI (%)
Raw CP	2.05	6.10	91.85	46	2.07
RF-CP	0.08	5.95	93.97	33	0.08

By the Friedel-Crafts reaction, the functional CP (DK-CP-1, 2, and 3) with diketone (-COCO-) exhibited a range of cross-linking bridges between the polycyclic aromatic hydrocarbons and the higher intensity of the C=O stretching peak (1760 cm^{-1} and 1735 cm^{-1}) as confirmed *via* FTIR spectra. As outlined (Scheme 1), this appeared that the carboxylic tar pitch might be prepared with diketone functionalized pitch after oxidation and fine permeable carbons would at that point be gotten after the charring process. In this test, oxidation finished in solution and a combination of polycarboxylic corrosive (or anhydride) was shaped. Dense sintering of the tar pitch and its functional derivatives were then conducted to notice different porous structure formations. Peak changes of C=O stretching were found around 1740 cm^{-1} (-COOH), which formed the best evidence for tracing the presence of diketone and its cleave. The cleavage mechanism of diketone might be explained by the key carbonyl methylene condensation during the charring process. The IR spectra showed that the diketone group of functional tar pitch was a constant process of change and the subsequent scanning electron microscopy (SEM) demonstrated its strong influence upon pore formation in charring. For the case, other precursor starting with carboxylic tar pitch but appeared differently for CP with a diketone group. The decarboxylation of carboxylic derivatives was conducted at 200 to 300°C and its mechanism had been suggested[17,18]. The carbonation of pitch and its derivatives could be accessible to the elastic-plasticide formation phase above 200°C and the decarboxylation of carboxyl polycyclic aromatic rings was favorable for the generation of hierarchical mesoporous carbons.

Results and Discussion

To simulate decarboxylation of carboxyl tar pitch, stearic acid as a lead compound was put to heating under atmospheric nitrogen, and the process of thermal gravimetric was carried out to 600°C. Thermal gravity-differential analysis and NMR spectrum were used for a superior understanding of the influence on the pore generation of carboxyl tar pitch (Fig. 1). Other studies have been reported that the high-temperature pyrolysis would take place in the decarboxylation of the carboxyl group. Thermal analysis of stearic acid showed that it began to decompose at 220°C. The structure of stearic acid and its decomposed product above 200°C were characterized by ^{1}H NMR and found its decarboxylation. It ensures that warm decarboxylation occurred first followed by the carbonation response at that point in continuity by raising the pyrolysis temperature.

In this study, a pyrolytic method of pitch and its subordinate was proposed to create the porous carbons, and TG/DTG, as well as SEM investigation, was utilized for characterizing porous structures within the pyrolysis processes. The results showed (Fig. 2A) that these pitches displayed extraordinary contrasts and the carbon from crude tar pitch endured loss of mass of up to 80 wt% around 800°C. From Fig. 2B, it would promptly be watched that the rough tar pitch displayed a distinct DTG peak at the early stage, this may be due to dissipation and refining of light compounds. The charring process of the functional tar pitches with diketone or carboxylic

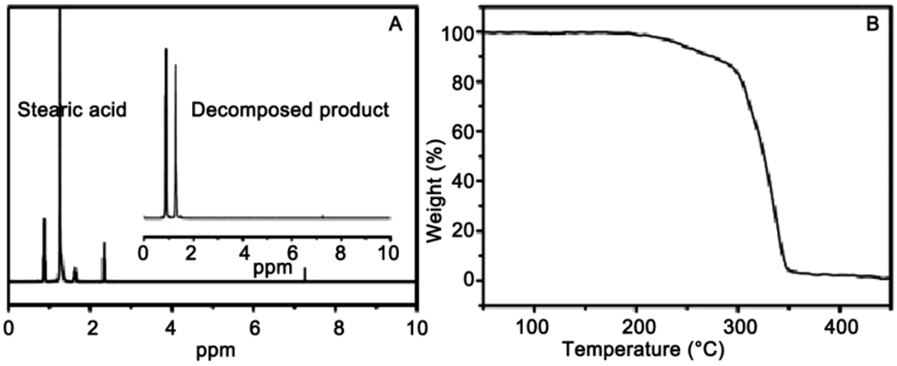


Fig. 1 — (A) ^{1}H-NMR spectra of stearic acid and its decomposer above 200°C and (B) Thermogravimetric analysis (TGA) curves of stearic acid

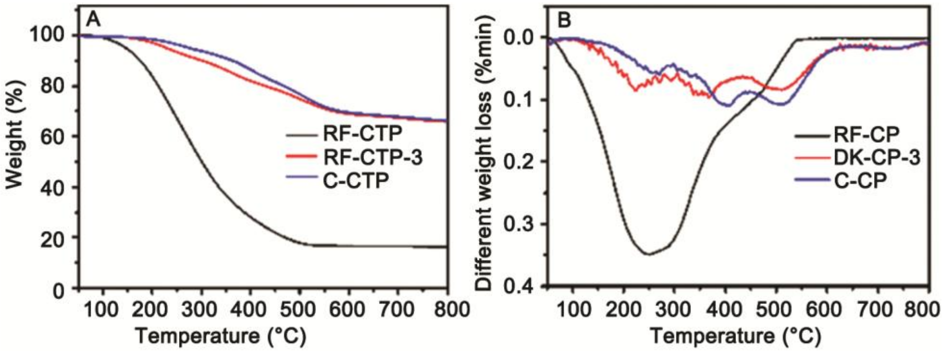


Fig. 2 — (A) TG and (B) DTG curves of tar pitch and its derivatives

bunch would endure low weight loss (35 wt%, 800°C) due to their functionalization and the carbonyl methylene condensation of aromatic aldehydes. The outcome of the thermal examination exhibited that the functional tar pitches with diketone or carboxylic group would have a relative debilitating inclination for a deferred thermal decomposition, and the shifted DTG peaks were seen at higher temperatures. It is possible to assume that the aromatic aldehydes would affect their thermal decomposition and the pore generation as well.

Surface morphology of HPCs

To characterize the prepared porous carbons, their morphology was studied by SEM analysis. The surface morphology and pore size of the manufactured carbons showed porous nanostructures. All the results are shown in Fig. 3 and these carbons differed from each other concerning their pore structures and surface morphology Concerning DK-CP-3, compact and lose aggregations of nanoparticles led by the cross-linkage reaction of polyaromatic hydrocarbon nanoparticles were experienced. Many mesopores and macropores, which were different from that of HPC-DK-3, HPC-RF, and HPC-C were found. Moreover, only block structures of the filtered CP after carbonization were observed, and both mesopore and macropore structures emerged in their matrix as carboxylic acid groups, which were introduced during the oxidation of diketone. The results also exhibit that the decarboxylation of carbonyl-functional CP is one of the core factors of its porous nanostructures; also the carboxyl content was a main governing index. Many studies demonstrated that mesoporous carbons displayed electrochemical capacitor functionality in many ways due to their unique structures.

The pore structure of HPCs

To differentiate the porous structures, the carbons from CP and its carbonyl-functional derivatives were checked with N_2 adsorption-desorption isotherms, and the results are presented in Fig. 4A. Compared to carbon carbonized with crude pitch, the porous carbons from the deionized pitch (HCP-DK-1,2,3) or carboxylated pitch (HCP-C) showed a hysteresis loop at medium pressure (P/P_0 = 0.4-0.7), signifying the formation of many mesopores. Besides, a quick increase in the high-pressure region (P/P_0 = 0.8-1.0) indicated that the adsorption and desorption isotherms occurred concurrently, with the manifestation of macropores[19,20]. The results also portrayed that

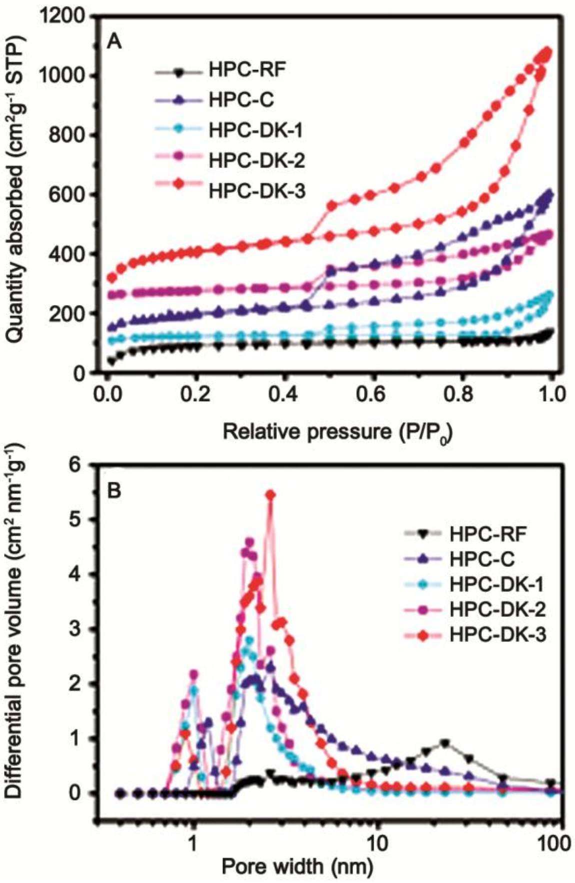


Fig. 4 — (A) N_2 absorption/desorption isotherms and (B) pore size distributions of HPC samples

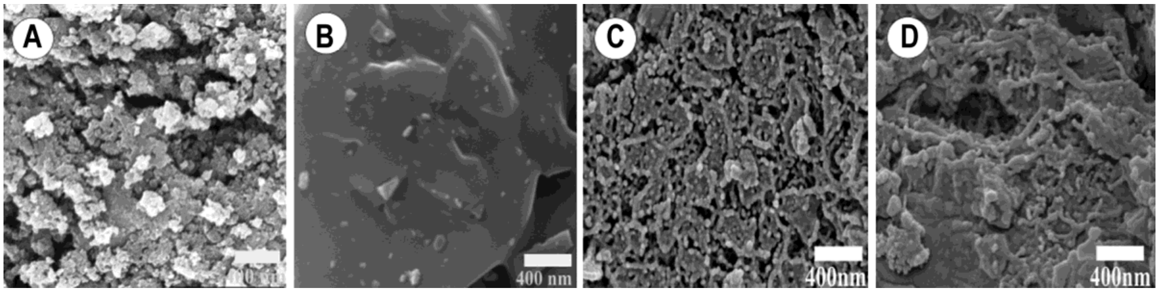


Fig. 3 — SEM images of (a) DK-CP-3, (b) HPC-RF, (c) HPC-DK-3 and (d) HPC-C

Table 2 — Pore structure parameters of samples

Samples	S_{BET} (m^2g^{-1})	S_{meso} (m^2g^{-1})	V_{total} (cm^3g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})
HPC-RF	43.1	34.9	0.06	0.003	0.057
HPC-DK-1	506.7	268.5	0.84	0.22	0.52
HPC-DK-2	865.6	473.1	1.04	0.27	0.77
HPC-DK-3	1277.3	740.3	1.45	0.33	1.12
HPC-C	649.6	317.1	0.76	0.20	0.56

carboxyl-functionalized or deionized pitch enhanced the crossing process of aromatic rings with carbonyl methylene condensation. The presentation of diketone functional groups is the key to the realization of the high cluttered carbon structure. The introduction of oxygen led to the cross-linking of the DK-CP structure, which prevented the softening and ordered the reorganization of DK-CP in the high-temperature carbonization process and restrained the graphitization process. Hence, under the condition of large OC/RFCP, BET has a larger surface area and pore volume, which can be deciphered as the result of a high degree of cross-linking. When the diketone group was decomposed to a carboxyl group, the cross-linking degree of RFCP decreases and Thermal decarboxylation is useful to the formation of pore structure in its access to the elastic-plastic deformation phase, which occurred above 200°C.

The curves of pore size distribution are shown in Fig. 4B. Carbon-based HPC-DK has a big pore structure and the structures of HPC-C and HPC-RF with mesopores (2-4 nm) and micropores structure (1-2 nm) would be favorable for their performance in the electrochemical process. Table 2 shows a summary of the pore structure parameters and the significance of carbonylation of the pitch. If a raw pitch was used only then, the porous carbon would be obtained with a lamellar structure, exhibiting lower pore volume and surface area. Via functionalization of diketone, the corresponding modified pitch displayed controlled carbonization and the pyrolysis process would be affected by its functionality. When the mass percentage of oxalyl chloride and raw pitch increased from 0.3 to 0.9, the obtained porous carbons showed a growing tendency for micropore structures and pore volume would increase from 506.7 to 1277 m^2g^{-1}. Therefore, experimental results also indicated that he obtained a porous carbon-based decarboxylated pitch exhibited a fine porous structure, indicating that improvements had been achieved.

Electrochemical properties of HPCs

While the hydrophilic polar groups were introduced into the CP, the lamellar structure was interrupted and may have the potential application in producing high-specific capacity electrodes for EDLC. Due to the π–π conjugation bonds of aromatic molecules, it strongly attracts the aggregation of nearby molecules. Therefore, the electro-capacitive performances were compared between carbons charred with functional pitches carrying either the carboxyl or the diketone group. A controlled microstructure of the obtained porous carbon was observed for the pitch containing either diketone or carboxyl groups, and their cyclic voltammetry (CV) curves showed quasi-rectangular shapes at scan rates of up to 50 mV s^{-1} (Fig. 5A). In contrast, the carbonized sample of the raw pitch showed a lamellar structure with low pores and weaker electrochemical characteristics (not shown). Evaluate the specific capacitance of the carbonized materials from the discharge curve, and was found to be highly dependent on the microstructure (Fig. 5B). HPC-DK-3 exhibited the highest capacitance of 273.4 F g^{-1} with a current density of 0.5 A g^{-1} in a symmetrical two-electrode cell, which far exceeded that of HPC-C (205.5 F g^{-1}) under the same conditions. As mentioned above, the performances of carbon-based supercapacitors were influenced both by surface area and pore size considerably. The low specific capacitance of HPC-C could be attributed to its low surface area (S_{BET} = 649.6 m^2 g^{-1}), thus limiting the accessible surface. Nyquist plot and cycle performance measurements were applied to determine carbonized samples and their major characteristics are summarized in Fig. 5C. The obtained porous carbons with diketone functional pitch exhibited better electrochemical properties, which was mainly due to its fine porous structure, which could be elucidated by the electric double-layer charge storage mechanism[21]. In contrast, porous carbons obtained with carboxyl pitch displayed a smaller semi-circle in the high-frequency region in the Nyquist plot test, indicating a low charge transfer resistance. The test results confirmed that all obtained porous carbons were validated as a double-layer mechanism in the low-frequency region, while their specific capacitances remained above 92% of its original value after 5000 consecutive cycles (Fig. 5D). The obtained porous carbon with diketone functional pitch showed better stability of its higher specific surface area and fine mesoporous structures.

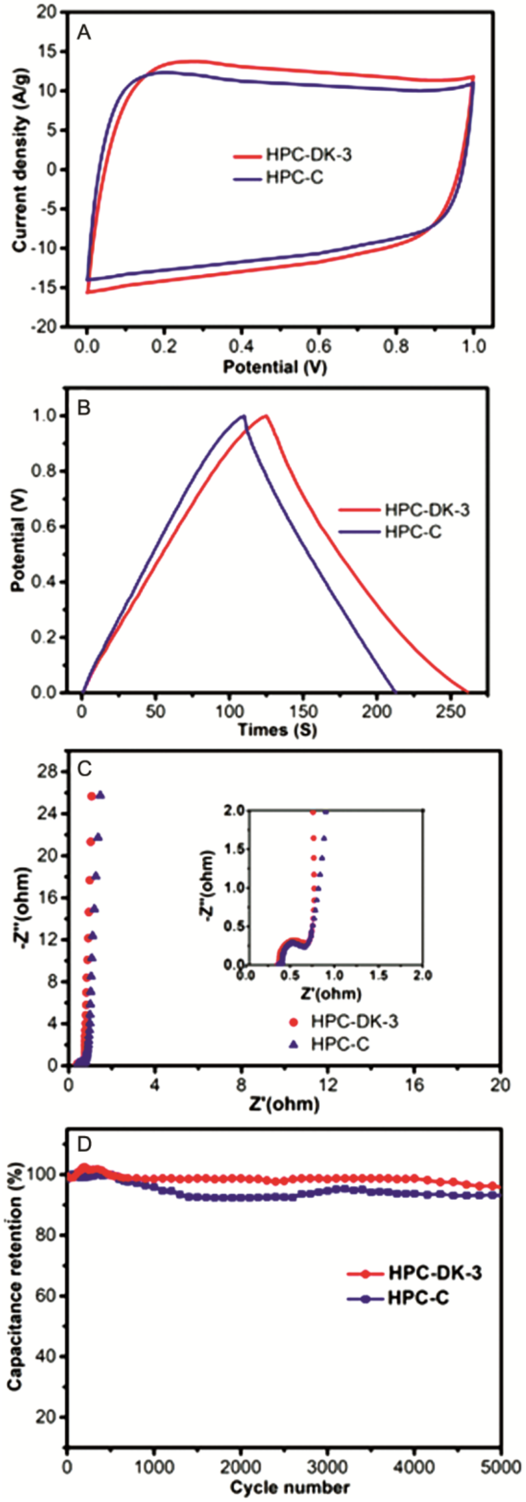


Fig. 5 — Electrochemical properties of carbonized materials. (A) CV curves at 50 mV s^{-1}, (B) charge-discharge curves at 0.5 A g^{-1}, (C) Nyquist plots of the porous carbon electrodes with the inset showing the plots in the high-frequency region and (D) Cycling stability of functional pitch electrode measured for 5000 cycles at a current density of 3.0 A g^{-1}

Conclusions

A facile and universal method for the combination of ordered mesoporous carbon materials from the modified pitches via carboxylation or modified by diketone has been developed. In a typical process, pitches were functionalized by the Friedel-Crafts reaction and via oxalyl chloride introducing the -COCO- bridges were introduced, and carboxylation was achieved via oxidation. The obtained porous carbons were charged with carboxylate pitch or -COCO- bridges, and the products exhibited fine porous structures and displayed better performance during the electrochemical measurements. By introducing diketone groups, the functional pitch exhibited a well-defined pore structure, and after charring, the porous carbon showed good electro-capacitive performance. For the carboxylation pitch, the obtained porous carbons also showed a controlled microstructure and exhibited better stability in its higher specific surface area and fine microporous structures. In contrast, carbonized samples with raw pitch showed a lamellar structure with low porosity that offered weaker electrochemical characteristics.

Conflict of interest

The authors declare no conflict of interest in this study.

References

1 Zhai Y, Dou Y, Zhao D, Fulvio PF, Mayes RT & Dai S, *Adv Mater*, 23 (2011) 4828.
2 Li X, Zhang Z, Yin K, Yang L, Tachibana K & Hirano SI, *J Power Sources*, 278 (2015) 128.
3 Elliot A, *Chem Commun*, 52 (2016) 11768.
4 Kim HW, Yoon HW, Yoon SM, Yoo BM, Ahn BK, Cho YH, Shin HJ, Yang H, Paik U, Kwon S & Choi JY, *Science*, 342 (2013) 91.
5 Lv Y, Gan L, Liu M, Xiong W, Xu Z, Zhu D & Wright DS, *J Power Sources*, 209 (2012) 152.
6 Ma X, Liu M, Gan L, Zhao Y & ChenL, *J Solid State Electrochem*, 17 (2013) 2293.
7 Wang Q, Yan J, Wang Y, Wei T, Zhang M, Jing X & Fan Z, *Carbon*, 67 (2014) 119.
8 Simon P, Gogotsi Y & Dunn B, *Science*, 343 (2014) 1210.
9 Lu C, Xu S, Wang M, Wei L & Liu S, *Carbon*, 45 (2007) 206.
10 Li T, Bo H, Cao H, Lai Y & Liu Y, *Int J Electrochem Sc*i, 12 (2017) 3099.
11 Na R, Su CW, Su YH, Chen YC, Chen YM, Wang G & Teng H, *J Mater Chem A*, 5 (2017) 19703.
12 Zhong C, Deng Y, Hu W, Qiao J, Zhang L & Zhang J, *Chem Soc Rev*, 44 (2015) 7484.
13 Moyo B, Momodu D, Fasakin O, Bello A, Dangbegnon J & Manyala N, *J Mater Sci*, 53 (2018) 5229.

14 Xu J, Wang X, Wang X, Chen D, Chen X, LiD & Shen G, *Chem Electrochem*, 16 (2014) 975.
15 Li W, Zhang A, Gao H, Chen M, Liu A, Bai H & Li L, *Chem Commun*, 52 (2016) 2780.
16 Wang P, Hu J, Cao G, Zhang S, Zhang P, Liang C, Wang Z & Shao G, *Appl Surf Sci*, 435 (2018) 1150.
17 Tripathi AK, Verma YL & Singh RK, *J Mater Chem A*, 3 (2015) 23809.
18 Alcaniz-Monge J, Cazorla-Amoros D& Linares-Solano A, *Fuel*, 80 (2001) 41.
19 Wan C, Yuan L & Shen H, *Int J Electrochem Sci*, 9 (2014) 4024.
20 Guo Y, Shi ZQ, Chen MM & Wang CY, *J Power Sources*, 252 (2014) 235.
21 Wang L, Wang J, Jia F,Wang C & Chen M, *J Mater Chem A*, 1 (2013) 9498.