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Ionic liquid C16mimBF4 assisted synthesis of poly(benzoxazine-co-resol) based hierarchical porous carbons with superior performance in supercapacitors



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#### Broader context

# Supercapacitors have emerged as the most promising candidates for energy storage as they can provide a higher power density than batteries. Porous carbon materials with high surface area, controlled pore size and excellent electrical conductivity have been widely used as supercapacitor electrode materials. We report herein a self-assembly approach of poly(benzoxazine-*co*-resol) with ionic liquid $C_{16}$ mimBF<sub>4</sub> for the fabrication of a hierarchical porous carbon monolith with a nitrogen and boron co-doped and local graphitized carbon framework. The nanostructures with graphitization and heteroatoms significantly improve the capacitance performance, exhibiting a superior high gravimetric capacitance of 247 F g<sup>-1</sup> and especially a higher interfacial capacitance of 66 $\mu$ F cm<sup>-2</sup>, achieving 96.2% capacitance retention after a 4000 long cycle life. Such boron and nitrogen co-doped porous carbon thus shows promise as an electrode material for supercapacitors. This synthesis method also broadens the avenue for one-pot synthesis of heteroatom doped carbon materials as high performance electrode materials.

#### 1 Introduction

Supercapacitors are considered to be the most promising energy storage and power output technologies for portable electronics, electric vehicles, and renewable energy systems.<sup>1,2</sup> With particular potential in electric vehicles, these systems are believed to play an important role in complementing or replacing batteries in the energy storage field. Porous carbons are indispensable candidates as supercapacitor electrode

#### materials due to their high surface area, chemical stability, lowcost, fine conductivity and many available forms.<sup>3,4</sup> The performance of supercapacitors strongly depends on the textural properties of the porous carbon electrodes, such as surface area, surface functionality, pore size distribution, tortuosity of pores, and degree of crystallinity. It has been shown that modification with electron-donating or electronwithdrawing elements on carbon skeletons, such as N,<sup>5–7</sup> B,<sup>8,9</sup> P<sup>10</sup> and O,<sup>11</sup> can modulate the electronic properties of the carbon and produce additional functional groups on the carbon surface, resulting in an enhancement in the electrochemical performance.<sup>11–13</sup> In general, post-modification processes are

simple but uncontrollable in terms of both the amount and

distribution of dopants.<sup>10</sup> For example, inorganic acids such as

boric acid or phosphoric acid have been used as a heteroatom

# Ionic liquid C<sub>16</sub>mimBF<sub>4</sub> assisted synthesis of poly(benzoxazine-*co*-resol)-based hierarchically porous carbons with superior performance in supercapacitors†

De-Cai Guo, Juan Mi, Guang-Ping Hao, Wei Dong, Guang Xiong, Wen-Cui Li and An-Hui Lu\*

Hierarchically porous carbons with variable pore sizes at multi-length-scale, a nitrogen and boron co-doped and local graphitized framework, and high mechanical strength were synthesized through the selfassembly of poly(benzoxazine-co-resol) with ionic liquid  $C_{16}$ mimBF<sub>4</sub> and a carbonization process. In this synthesis, the ionic liquid acts both as a structure directing agent and a heteroatom precursor. The obtained porous carbons have a specific surface area lower than 376 m<sup>2</sup> g<sup>-1</sup> and thus a high skeleton density. With such heteroatom doped skeleton structures and fully interconnected macropores, mesopores and micropores, the hierarchically porous carbon shows outstanding electrochemical performance, e.g. a superior high gravimetric capacitance ( $C_g$ ) of 247 F g<sup>-1</sup>, an interfacial capacitance ( $C_s$ ) of 66  $\mu$ F cm<sup>-2</sup> (calculated based on the discharge curve with a constant current density of 0.5 A g<sup>-1</sup>), whilst a high volumetric capacitance ( $C_v$ ) of 101 F cm<sup>-3</sup> compared to those reported in the literature. Cycling stability tests indicate that the carbon exhibits a capacitance retention of ~96.2% after 4000 charge–discharge cycles, strongly reflecting an excellent long-term cyclability of the electrode. Due to its unique skeleton structure and high conductivity, such hierarchically porous carbon shows promise as an electrode material for supercapacitors.

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State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P.R. China. E-mail: anhuilu@dlut.edu.cn; Fax: +86 411-84986112; Tel: +86 411-84986112

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precursor for the preparation of B or P doped carbons. However, due to the different intrinsic properties of inorganic acids and organic framework, the doped heteroatoms are rather heterogeneous in distribution.<sup>14</sup> Alternatively, direct incorporation of heteroatoms into the carbon precursors prior to carbonization can yield a homogeneous distribution of heteroatoms in a carbon framework.

Ionic liquids (ILs) generally inherit many excellent features, such as good solubility for chemicals, excellent thermal stability and negligibly small vapor pressure. Antonietti15 and Dai et al.<sup>16</sup> have employed ILs containing nitrile groups as carbon precursors via cyclotrimerization to form a triazine network and then poly(ionic liquid)s, which can be converted to N-doped porous carbon materials under pyrolysis conditions. In this case, only the ionic liquids containing crosslinkable functional groups can be used as carbon precursors and the carbon yield is relatively low. In contrast, carbonization of ILs without any cross-linkable functional groups affords no carbon produced. Taking advantage of ILs, we are attempting to use ILs as a heteroatom source for a doping agent during the polymerization of carbon precursors, which may not only facilitate the solubility of carbon precursors (in the current cases, organic molecules), but may also serve as a heteroatom source for a doping agent. The IL C<sub>16</sub>mimBF<sub>4</sub> was chosen as a B- and N-containing precursor for the preparation of poly(benzoxazine-co-resol)-based monolithic carbons. C16mimBF4 together with surfactant F127 were added into the benzoxazine-co-resol (resorcinol, formaldehyde and 1,6diaminohexaneamine) self-assembly polymerization system. It has been previously shown that the polybenzoxazine and surfactant F127 can form mesostructure assembly via hydrogen bonds.<sup>17</sup> In principle, the anions of C<sub>16</sub>mimBF<sub>4</sub> and the polybenzoxazine segments can interact in a form of Ar-Hvia hydrogen bonds. Thus, the ionic liquid  $O \cdots BF_4^{-}$ C<sub>16</sub>mimBF<sub>4</sub> will be homogeneously distributed in the polymer and carbon skeleton. As a result, an improved electrochemical performance of such carbon as an electrode material can be expected.

#### 2 Experimental sections

#### 2.1 Chemicals

Resorcinol (99.5%) and formaldehyde (37 wt% solution) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. 1,6-Diaminohexane (99.0%), ethanol (99.7%), 1-methylimidazol (99.5%), sodium tetrafluoroborate (99.5%) and 1-hexadecyl chloride (99%) were all supplied by Sinopharm Chemical Reagent Co., Ltd. Pluronic F127 was purchased from Sigma-Aldrich. All chemicals were used as received.

#### 2.2 Synthesis of N-, B-co-doped porous carbons

Ionic liquid  $C_{16}$ mimBF<sub>4</sub> was first synthesized as described.<sup>18,19</sup> Typically, 1-hexadecyl chloride was mixed with 1-methylimidazole and refluxed at 90 °C for 24 h. Afterwards, the collected product  $C_{16}$ mimCl was redispersed into tetrahydrofuran (THF) for recrystallization and then mixed with NaBF<sub>4</sub> aqueous solution. After filtration, washing and drying steps, tetra-fluoroborate salt ( $C_{16}mimBF_4$ ) was obtained.

For the synthesis of porous carbon, 0.5 g of resorcinol (R) and 0.209 g of Pluronic F127 were dissolved in a mixed solvent of ethanol (1.5 g) and deionized water (1.5 g). Afterwards, 0.088 g of  $C_{16}$ mimBF<sub>4</sub> and 0.026 g of 1,6-diaminohexane (DAH) were successively added to the above solution. Subsequently, 0.736 g of formaldehyde (F) solution was injected into the solution. The reaction system instantaneously (<1 min) turned to a white homogeneous emulsion. This emulsion was then sealed and transferred into an oven at 90 °C. It quickly solidified within 15 min. This gel was cured for an additional 4 h.

The as-made polymer monolith was first dried at 50 °C and followed by pyrolysis at 800 °C for 2 h under a nitrogen atmosphere to obtain a crack-free porous carbon monolith (denoted as CNB-1). By varying the amount of  $C_{16}$ mimBF<sub>4</sub>, different carbon monoliths were prepared and labeled as CNB-*x*, where *x* indicates the different amounts of the ionic liquid  $C_{16}$ mimBF<sub>4</sub> used. For comparison, one sample (denoted as CN) without the use of ionic liquid was also prepared. In all syntheses, the molar ratio of R/F127 was fixed at 275 : 1 and R/F at 1 : 2. The mass ratio between water and ethanol was fixed at 1 : 1. The synthesis conditions are listed in Table 1.

#### 2.3 Characterization

Scanning electron microscopy (SEM) investigations were carried out with a FEI Nova NanoSEM 450 instrument. Transmission electron microscopy (TEM) images were obtained with a FEI Technai F30 equipment operating at 300 kV. The samples for TEM analysis were prepared by dropping an ethanol droplet of the products on carbon coated copper grids and drying at room temperature. Nitrogen and carbon dioxide  $(CO_2)$  adsorption isotherms were measured with an ASAP 2020 sorption analyzer (Micromeritics). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas  $(S_{\text{BET}})$ . Pore size distributions (PSDs) were determined from the adsorption branches of the isotherms using density functional theory (DFT) for micropores and the Barrett-Joyner-Halenda (BJH) model for mesopores. Total pore volumes  $(V_{total})$  were calculated from the amount adsorbed at a relative pressure  $P/P_0$  of 0.97. Micropore volumes  $(V_{\text{micro}})$  were calculated using the *t*-plot method. The X-ray diffraction (XRD) measurements were taken on a Rigaku D/Max 2400 diffractometer using Cu  $K_{\alpha}$  radiation (40 kV, 100 mA,  $\lambda = 1.5406$  Å). Raman spectra were collected on a homemade DL-2 microscopic Raman spectrometer, using a 532 nm line of a KIMMON laser. The electron conductivity was tested by a four point probe setup of RTS-9 (Guangzhou Four Probe Technology Co., Ltd.). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-1600 ESCA (VG Scientific, UK) using a monochromatic Mg Ka excitation source. The quantitative analysis was conducted with multipark software after background subtraction. Infrared microspectroscopy investigations were carried out with a Nicolet iN10 (Thermo scientific Co., Ltd., USA) by averaging 64 scans in the 4000-670 cm<sup>-1</sup> spectra range at 4 cm<sup>-1</sup> resolution. Elemental analysis was carried out on a CHNO elemental analyzer (Vario EL III,

Table 1 Synthesis conditions and properties of porous carbons

Sample	Molar ratio of R/ionic liquid/F127/amine	$S_{ m BET} \ (m^2  g^{-1})$	D <sub>peak</sub> (nm)	$V_{\text{total}}$ (cm <sup>3</sup> g <sup>-1</sup> )		$V_{ m mic}/V_{ m total}$ (%)	ho (g cm <sup>-3</sup> )	$egin{array}{c} C_{ m g}{}^a \ ({ m F}~{ m g}^{-1}) \end{array}$	$C_{ m s}^{\ b}$ (µF cm <sup>-2</sup> )	$C_{\rm v}^{\ c}$ (F cm <sup>-3</sup> )
CN	275:0:1:13.6	596	6.6	0.36	0.20	55.6	0.19	182	30.5	35
CNB-1	275:13.2:1:13.6	529	6.5	0.36	0.19	52.8	0.21	199	38	42
CNB-2	275:26.4:1:13.6	497	6.5	0.33	0.18	54.5	0.28	177	36	50
CNB-3	275:39.6:1:13.6	376	5.8	0.24	0.15	62.5	0.41	247	66	101
CNB-4	275:79.2:1:13.6	373	$2.1^d$	0.20	0.15	75.0	0.45	154	41	69

<sup>*a*</sup> The gravimetric capacitance was calculated from GC curves at a current density of 0.5 A g<sup>-1</sup> in a three electrode system using  $C_{\rm g} = (I\Delta t)/(m\Delta V)$ ,<sup>20</sup> where I(A),  $\Delta t$  (s),  $\Delta V$  (V) and m (g) are the discharge current, the discharge time, the potential window from the end of the voltage drop to the end of the discharge process and the mass of two electrodes, respectively. <sup>*b*</sup> Interfacial capacitance was calculated as  $C_{\rm s} = C_{\rm g}/S_{\rm BET}$ ,  $S_{\rm BET}$  is the specific surface area of the sample. <sup>*c*</sup> Volumetric capacitance was calculated as  $C_{\rm v} = \rho C_{\rm g}$ ,  $\rho$  is the density of the active material. <sup>*d*</sup> Use adsorption average pore width.

Elementar). The weight ratio of boron was determined through inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, Optima 2000 DV ICP-OES). The mechanical properties of the samples were tested under uniaxial compression using a 2 kN intelligent strength tester (model DL III, Dalian Research & Design Institute of Chemical Industry). The compressive strength is the maximum stress supported by the samples during the test, *i.e.*, the stress at which macroscopic failure occurs. Tests were performed at a strain rate of 1 mm min<sup>-1</sup>. All measurements were recorded at *ca.* 25 °C and 70% relative humidity. Samples were of cylindrical shape, carefully machined to ensure perfectly parallel bases and had a length/ diameter ratio of 1.

#### 2.4 Electrochemical measurements

The working electrodes were prepared by mixing 85 wt% porous carbons as the active materials, 15 wt% polytetrafluoroethylene (PTFE) in 7 mL ethanol. No any other conductive agent was used. The slurry of the mixture was rolled into a film, cut into suitable shapes and placed into an oven at 150 °C for 4 h. The films were then put onto a foam nickel current collector with an area of 1 cm<sup>2</sup> and finally pressed under a pressure of 10 MPa for 5 min to fabricate an electrode. The mass loading of the active material was in between 4 and 6 mg  $cm^{-2}$ . The capacitive performance of the single electrode was carried out on an CHI660D electrochemical workstation (CH Instruments Inc., Shanghai, China) using a standard three-electrode test system composed of Hg/HgO as a reference electrode and a Pt plate as a counter electrode in 6 M KOH electrolyte at 25 °C. Cyclic voltammetry (CV), alternating current impedance and galvanostatic charge-discharge cycling (GC) measurements were employed in the evaluation of the electrode electrochemical performance. The capacitance of the supercapacitor cell of the carbon was calculated by the following equation:  $C_{\text{cell}}(\text{F g}^{-1}) = \frac{I\Delta t}{m\Delta V}$ , where *I* (A),  $\Delta t$  (s),  $\Delta V$  (V) and *m* (g) are the discharge current, the discharge time, the operation potential window from the end of the voltage drop to the end of the discharge process and the total mass of two electrodes, respectively.20

#### 3 Results and discussion

Through a self-assembly of poly(benzoxazine-co-resol) assisted by ionic liquid C16mimBF4 and a carbonization process, a series of hierarchical porous carbon monoliths were obtained. The porous structures of the carbon monoliths were characterized by N<sub>2</sub> adsorption at 77.4 K. As seen from Fig. 1a, the isotherms of samples CNB-1 to 3 exhibit a typical type IV shaped curve with a type H2 hysteresis, which are attributed to a predominantly mesoporous structure.<sup>21</sup> The isotherm of CNB-4 however exhibits a typical I curve, which is an indication of a microporous structure only. It is evident that the capillary condensation relative pressure range  $(P/P_0)$  for CNB-3 is lower than that for CNB-1 and CNB-2. The pore size distributions (PSDs) presented in Fig. 1b show similarities in the pore structures of CNB-1 and CNB-2, whose mesopores are concentrated at  $\sim$ 6.5 nm, but the PSD of CNB-3 is slightly broader and with a smaller average pore size  $\sim$ 5.8 nm. As the amount of ionic liquid increases, the specific surface areas of samples from CNB-1 to CNB-4 decrease



**Fig. 1** N<sub>2</sub> isotherms of the porous carbon (a) and their corresponding PSDs (b). The isotherms of CNB-1, CNB-2 and CNB-3 were offset vertically by 60, 50 and 50 cm<sup>3</sup> g<sup>-1</sup> STP, respectively. The CO<sub>2</sub> sorption isotherm of CNB-3 at 0 °C (c) and the corresponding PSD (d).

from 529 to 373 m<sup>2</sup> g<sup>-1</sup>, and the pore volumes decrease from 0.36 to 0.20 cm<sup>3</sup> g<sup>-1</sup>. The volume ratio of micropore to total pore volume increases from 53% to 75% (see Table 1). Clearly, the more  $C_{16}$ mimBF<sub>4</sub> used in the synthesis, the more developed microporosity.

To further assess the ultramicropores (pores width <1 nm), as an example, the CO<sub>2</sub> adsorption isotherm of sample CNB-3 was measured at 0 °C, as seen in Fig. 1c. A nonlinear density functional theory (DFT) analysis of the CO<sub>2</sub> adsorption isotherm showed that the width of the micropores was predominantly in the range of 0.45–0.61 nm (Fig. 1d). These micropores should be suitable for the diffusion of electrolyte ions (ion size of solvated K<sup>+</sup>: 0.36–0.42 nm, greater than OH<sup>-</sup>).<sup>22,23</sup> The good match between the pore size and the radius of electrolyte ions is potentially helpful for an enhancement of the utilization of the effective specific surface area for supercapacitors.<sup>24</sup>

The SEM observation on the resultant carbon monoliths reveals (Fig. 2) that the carbon possesses a continuous spongelike branched framework and fully interconnected macropores ranging from 10 to 50  $\mu$ m. The inset images in Fig. 2 show that the carbon skeleton has continuous mesopores and macropores whose diameters vary from 10 to 200 nm. Variations in pore diameters of these samples are clearly evident, *e.g.* the pore sizes of CNB-1 and CNB-2 ranging from 50 to 200 nm, while those of CNB-3 and CNB-4 ranging from 10 to 100 nm. Such highly interconnected macropores and mesopores allow a fast transportation of electrolyte in the porous carbon by minimizing molecular diffusion limitation,<sup>25</sup> consequently ensuring a high rate capability.<sup>26</sup> As a comparison, the morphology change of CN can clearly be seen in Fig S1a (ESI<sup>†</sup>).

In general, for carbon based supercapacitors, a high surface area of carbon invariably leads to a high gravimetric capacitance, however, this is often at the expense of volumetric capacitance and a rate capability. So, it remains a great challenge to rationally synthesize porous carbons with a balance between the surface area and tap density in order to obtain both high gravimetric and volumetric capacitance simultaneously. In our synthesis, the bulk density values calculated by determining the weight in a fixed volume of the carbon monolith are listed in Table 1. With an increase in the IL amount, the bulk density values are enhanced from 0.19 to 0.45 g cm<sup>-3</sup>, which is higher than those (0.08–0.45 g cm<sup>-3</sup>) reported for carbon aerogels or mesoporous carbon.<sup>27</sup> The mechanical strength of monoliths CNB-3 and CNB-4 can bear corresponding loads of 1.73 and 5.63 MPa, which are significantly greater than that reported for a porous carbon monolith (~0.2 MPa).<sup>28,29</sup> This observation indicates that the addition of IL exerts a significant influence on the polymerization of carbon precursors and accordingly leads to a stout framework.

To characterize the local atomic structure, the samples were subjected to XRD analysis. As seen in Fig. 3a, the peaks were identified as a typical (002) interlayer peak of graphitic carbon at  $2\theta = 25^{\circ}$ , indicating that graphitic structures were developed to a certain extent. The values of  $d_{002}$  from CNB-1 to 4 are about 0.389 nm, larger than that of graphite (0.335 nm), suggesting a random combination of graphitic and turbostratic stacking. The pronounced peak at 43°, however, points to the formation of a higher degree of interlayer condensation of the samples. The local graphitic structures of the samples were further supported by Raman spectroscopy. As shown in Fig. 3b, the peaks observed at 1590 and 1350 cm<sup>-1</sup> are attributed to the G (stretching mode of graphite) and D (breathing mode) bands, respectively. From the TEM image of sample CNB-3 (Fig. 3c and d), one can see a short range ordering, *i.e.* three to four layers of graphene stacking. Combining the XRD, Raman and TEM results, we can deduce that the carbon monoliths synthesized with the assistance of ionic liquid  $C_{16}mimBF_4$  display a partial



Fig. 2 SEM images of CNB-1 (a), CNB-2 (b), CNB-3 (c) and CNB-4 (d).



**Fig. 3** Powder XRD patterns in the wide-angle region (a) and Raman spectra (b) for CNB-1, CNB-2, CNB-3 and CNB-4; TEM image (c) and high resolution TEM image (d) of CNB-3.

Table 2 Elemental compositions of the porous carbon monoliths

	Eleme	ental ana	alysis, w	B content, wt%		N content, wt%	
Sample	С	Ν	Н	0	ICP	XPS	XPS
CN	88.5	0.42	1.05	10.03	_	_	0.8
CNB-1	88.6	0.64	1.03	9.7	0.05	—	0.6
CNB-2	85.7	0.68	1.10	12.4	0.15	0.10	1.1
CNB-3	85.5	0.53	1.76	11.6	0.66	0.32	1.2
CNB-4	83.7	0.63	2.15	12.9	0.63	0.33	0.9

graphite-like microstructure, even at a moderate carbonization temperature of 800 °C. Compared to completely amorphous carbon, a locally graphitic structure can endow the as-prepared porous carbon monolith with good electrical conductivity.

Since the surface property of a carbon electrode also plays an important role in achieving high electrochemical performance, the surface and bulk composition of samples CN and CNB-1 to 4 were analyzed by XPS and elemental analysis (ICP-OES technique). The presence of both N and B on the carbon surface and bulk can be detected with an indication that the heteroatom of B in bulk is slightly higher than on the surface, contrary to what is observed for N (Table 2). The variation of the values can be explained by the surface specificity of XPS measurements. Since XPS is a surface sensitive technique, an enrichment of boron inside the material is also possible. From the XPS spectra of C1s (Fig. 4a), the most pronounced peak located at 284.6 eV (peak I) is characteristic of a carbon lattice (Table S1<sup>+</sup>), and the remaining peaks are C-OH and C-N (286.2 eV), C=O (288.2 eV), COOH (289.6 eV) and carbonate (291.2 eV) in sequence. Oxygen is commonly present in carbon as a consequence of its incorporation in the dangling bonds when the materials are exposed to air (Fig. 4b). Due to a limited nitrogen content, it is less

meaningful to fit which kinds of nitrogen-containing functional groups can be assigned on the carbon surface (Fig. 4c).

Based on the XPS analytic results in Table 2, it should be noted that the amount of oxygen, nitrogen and boron is improved from CNB-1 to 4, but reaching a maximum content for CNB-3. Obviously, boron-doping facilitates oxygen chemisorptions by showing an enhancement of oxygen content. Carbon oxidation and oxygen chemisorption are regarded as electrophilic reactions. The redistribution of  $\pi$  electrons in the presence of substituted boron and nitrogen weakens C–C bonds and strengthens C–O bonds upon oxygen adsorption.<sup>30</sup> A similar variation trend between the mass ratio of B and N on the surface and in the bulk indicates an identical distribution of B and N atoms. Therefore, the ionic liquid not only influences textural features but also plays a role in the introduction of heteroatoms homogeneously into the carbon framework through partial involvement in the condensation reaction of the synthesis.

The evolution of the chemical composition of the obtained carbon materials was further characterized by infrared microspectroscopy. Fig. 5 shows that the bands at *ca.* 3400 cm<sup>-1</sup> can be assigned to the presence of the O–H or N–H stretching vibration. The broad peak at ~1640 cm<sup>-1</sup> is assigned to the N–H in-plane deformation vibration and the broad medium strong bands ~900 cm<sup>-1</sup> correspond to the out-of-plane N–H deformation vibration.<sup>31</sup> The broad peak at approximately 1180, 1110 and 1009 cm<sup>-1</sup> can be assigned to the B–C stretching vibration,<sup>32</sup> and the band at 1310 cm<sup>-1</sup> can be assigned to the B–O vibration. The bands at 1540 cm<sup>-1</sup> and 1450 cm<sup>-1</sup> can be assigned to the C=C stretching vibration in the aromatic rings. Hence, the IR analysis confirms the existence of N- and B-containing functional groups.

It is noteworthy that the conductivities of the samples are higher than the values of the ordinary mesoporous carbons and activated carbons reported in the literature  $(0.2-2 \text{ S cm}^{-1})$ .<sup>33</sup>



Fig. 4 XPS spectra: fitted C1s spectrum (a), O1s spectrum (b), and N1s spectrum (c) for CNB-1, CNB-2, CNB-3 and CNB-4.



Fig. 5 IR spectra of the obtained carbon materials of CN, CNB-1, CNB-2, CNB-3 and CNB-4.

Remarkably, the conductivities of CNB-3 and CNB-4 can reach 2.52 and 4.33 S cm<sup>-1</sup>, respectively. This should be attributed to the local graphite-like microstructure and the N, B co-doped multi-length-connected carbon framework, which can facilitate the transmission of electrons by increasing the conductivity. The high conductivity of these structures prompted us to evaluate them as electrodes for supercapacitors.

Fig. 6a and b show the CV curves of samples CNB-1 to 4 at a scan rate of 5 mV s<sup>-1</sup> in 6 mol L<sup>-1</sup> KOH electrolyte, as well as the GC profiles at a current density of 0.5 A g<sup>-1</sup>. All samples present symmetric and rectangular CV curves, and the GC curves are perfectly linear for all porous carbon monoliths, indicating an approximately ideal electric double-layer capacitance performance and good stability of the electrolyte in this operating voltage range. The small 'humps' in the CV curves at the potential of -0.5 V vs. Hg/HgO indicate that the heteroatoms have been successfully incorporated into the carbon framework. These humps (around -0.5 V) are not so obvious in a basic medium, probably due to the basic character of the functionality of B, N in these carbon materials.<sup>12</sup> The  $C_g$  values of



**Fig. 6** The CV curves tested at a scan rate of 5 mV s<sup>-1</sup> (a); the GC curves tested at a current density of 0.5 A g<sup>-1</sup> (b); Nyquist plots in the frequency range of 100 kHz to 10 mHz in KOH electrolyte at 25 °C (c); frequency response of the gravimetric capacitance of CNB-1 to 4 (d).

samples CNB-1 to 4 range from 154 to 247 F g<sup>-1</sup> (from the discharge curve with a constant current of 0.5 A g<sup>-1</sup>), and their corresponding  $C_{\rm s}$  values vary from 36 to 66  $\mu$ F cm<sup>-2</sup> (Table 1). Noticeably, CNB-3 presents the highest values in  $C_{\rm g}$  and  $C_{\rm s}$ , which are considerably higher than those reported in the literature (Fig. S2†) despite sample CNB-3 having a low specific surface area. The voltage drop of CNB-3 at the start of a discharge is 2.24 mV at a current density of 0.5 A g<sup>-1</sup>, suggesting a very low equivalent series resistance (ESR), good conductivity and the ability for a quick charge propagation.

The impedance measurement was further performed to evaluate the resistance. As seen in Fig. 6c and d, the intercept at the real impedance (Z') axis in the high-frequency region is related to internal resistance, which determined the power capability of a capacitor. CNB-3 and CNB-4 present a lower ESR, which is mainly attributed to the high electron conductivity resulting from the local graphitized framework of CNB-3 and CNB-4. As frequency decreases (Fig. 6c), there are no obvious semicircles for all tested carbon based supercapacitors, which demonstrates that the resistance between the electrolyte and the electrode is very low, resulting from the 3D hierarchical porous structure of the carbon materials. At the low frequency region (<1 Hz), the inclined lines for CNB-3 are close to the theoretical vertical line and show characteristic features of pure capacitive behavior, indicating the electrolyte can easily access the pores. As shown in Fig. 6d, the capacitance dependence on the frequency (10 mHz to 100 kHz) of the prepared carbonbased supercapacitors is compared. The supercapacitor prepared with CNB-3 exhibits a slow capacitance drop due to fast ion transport and quick ion adsorption on the surface. This result further confirms the importance of creating easy iontransport pathways in pursuit of high-rate supercapacitor electrodes.

The high performance of CNB-3 might be explained as follows: a boron atom has three valence electrons, being less than that of a carbon atom by one electron, and can introduce a hole charge carrier once it replaces a carbon atom in the carbon lattice. It thus can increase the charge density and further improve the double layer capacitance. In one word, the abovementioned results strongly indicate that porous carbon monolith CNB-3 might be an excellent candidate for supercapacitors.

Rate capability is an important factor for the utilization of supercapacitors in power applications. A good electrochemical energy storage device is required to provide high energy density (or gravimetric capacitance) at a high charge-discharge rate. Thus, CV tests at different scan rates and GC tests at different current densities for sample CNB-3 were conducted and are shown in Fig. 7. It can be seen that when the scan rate gradually increases from 5 to 500 mV s<sup>-1</sup>, a similar rectangular shape is retained (Fig. 7a and b), indicating a good capacitance performance at a high scan rate. Moreover, all GC curves show isosceles triangular shapes at current density ranging from 0.5 to 20 A  $g^{-1}$  (Fig. 7c and d), suggesting an ideal capacitor behavior even at high current density. Sample CNB-3 presents a high specific capacitance of 247 F  $g^{-1}$  at 0.5 A  $g^{-1}$ , and it retains the value high up to 167 F  $g^{-1}$  at 20 A  $g^{-1}$ . This excellent performance of such a porous carbon monolith is attributed to its 3D



**Fig. 7** The high rate capability performance of CNB-3 tested in a three electrode system at different scan rates and current densities.

aperiodic hierarchical porous structure and B, N co-doped continuous carbon framework.<sup>26</sup> It facilitates the ion transport, furthermore avoiding ion hopping among different particles in pore channels, and thus it contributes synergistically to the high-rate performance.<sup>34</sup> On the other hand, our results also indicate that boron and nitrogen dopants can modify the polarity of a carbon matrix by improving the wettability, and allow an easy diffusion of the electrolyte ions into micropores, as suggested in the literature.<sup>35</sup>

The cycling stability of heteroatom doped carbon as an electrode material during a charge–discharge process is another key factor, which needs to be considered for a practical application. Therefore the cycling stability of CNB-3 was investigated. As shown in Fig. 8a, the capacitance of CNB-3 approaches saturation after 500 cycles. During this period of cycle time, the carbon electrode was wetted well by electrolyte-ions. The capacitance retention of ~96.2% after 4000 charge–discharge



Fig. 8 The long cycle life of CNB-3 over 4000 cycle numbers (a), the first 10 cycles of GC curves (b), and the last 10 cycles of GC curves (c) tested at a current density of  $1 \text{ A g}^{-1}$  with a two electrode system.

cycles strongly indicates an excellent performance stability of the heteroatom doped carbons. The GC curves of the last 10 cycles retained an almost identical shape as the first 10 cycles (Fig. 8b and c) by maintaining their linearity and symmetry. This illustrates again that the CNB-3 electrode has a good electrochemical capacitance and excellent long-term cycle stability.

In consideration of a high gravimetric capacitance and superior rate performance, the volumetric capacitance, a crucial parameter for practical application, was further calculated by multiplying the gravimetric capacitance with the bulk density of sample CNB-3. Remarkably, the volumetric capacitance of CNB-3 can reach 101 F cm<sup>-3</sup>. It is very close to the previously reported CDC carbons from chlorine activated TiC  $(118 \text{ F cm}^{-3})^{36}$  and more than the microwave exfoliated GO which was activated by KOH ( $\alpha$ -MEGO) (60 F cm<sup>-3</sup>).<sup>4</sup> However, it is worth mentioning that our heteroatom doped carbons can be synthesized in a much simpler manner whilst showing excellent electrochemical performance. The high volumetric capacitance implies a superiorly high surface utilization in heteroatom doped carbons. For clarity, we made a comparison of the capability of heteroatom doped carbon nanostructures to enhance the  $C_{\rm g}$  and  $C_{\rm s}$ . These were summarized in Fig. S2, S3, and Table S2, S3.<sup>†</sup> As seen in Fig. S2 and S3,<sup>†</sup> though some carbon samples show similar  $C_{\rm g}$  values to that of CNB-3, the  $C_{\rm s}$ of CNB-3 is the highest among these previously reported carbons. Thus far, the above results highlight that such a selfassembly approach of poly(benzoxazine-co-resol) with ionic liquid is a powerful tool for the fabrication of heteroatom doped carbon materials for supercapacitors. The excellent performance of CNB-3 is particularly beneficial to the distinctive nanostructure which is derived from the purposive design for supercapacitor electrode materials.

#### 4 Conclusion

Using ionic liquid C<sub>16</sub>mimBF<sub>4</sub> as the additive, nitrogen- and boron-doped porous carbons with fully connected 3D hierarchical porosity and local graphitic texture were derived from poly(benzoxazine-co-resol) polymers. The use of C<sub>16</sub>mimBF<sub>4</sub> not only leads to boron incorporation in the framework but also modulates the microstructure of the carbon. The local graphitic heteroatom-incorporated carbon matrix presents a higher conductivity. Due to their exceptional nanostructure and surface characteristics, these materials demonstrate an excellent capacitance performance. In particular, sample CNB-3 has a high  $C_{\rm g}$  (247 F g<sup>-1</sup>),  $C_{\rm s}$  (66  $\mu$ F cm<sup>-2</sup>) and  $C_{\rm v}$  (101 F cm<sup>-3</sup>) at a constant current of 0.5 A g<sup>-1</sup>, with excellent longterm cyclability. We believe that this study may provide a new avenue for the development of novel heteroatom-doped carbon-based electrode materials, relying on modified benzoxazine chemistry in the presence of ionic liquids. This offers a high degree of flexibility in the molecular design of monomers and puts forward a new one-pot synthesis for the incorporation of multiple heteroatoms into a carbon matrix. This ensures wide applications of porous carbon materials in electrochemistry.

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