

PAPER

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Fine-regulating ultramicropores in porous carbon *via* a self-sacrificial template route for high-performance supercapacitors†

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Ultramicropores (size < 0.7 nm) are critically demanded to provide an efficient path for the penetration and transportation of electrolytes to achieve high-performance supercapacitors. Here, a self-sacrificial template approach is adopted, which introduces C8 alkyl chains with a kinetic diameter of 0.8–1 nm to occupy the cavity of a porous aromatic framework (PAF). During the heating process, the alkyl chains decompose from the dense architecture as the temperature increased from 500 to 600 °C, forming ~1 nm micropores. The newly-obtained cavities provide sites for thermal-driven skeleton engineering (700–900 °C) to obtain ultramicropores. Based on the well-defined pore structure, the carbonized PAF solid revealed outstanding electrochemical performances, including high rate and long-term stability in a 6 M KOH electrolyte. Notably, the specific capacitance (294 F g⁻¹) derived from the self-sacrificial template method exceeds the capability of all the other methods for the construction of ultramicropores including self-template strategy, carbonization of nanoparticles, and template-assisted strategy. The synthesis of ultramicroporous carbons *via* the self-sacrificial template route opens up a promising gate to adjust the porous structure for high-performance applications in supercapacitors.

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1. Introduction

Supercapacitors have become a hot spot in the research of energy storage devices for various advanced applications such as personal portable electronic devices, hybrid electric vehicles, and aerospace power sources.^{1–4} As the decisive part, superior electrodes are extensively studied and evaluated for better electrochemical performance of supercapacitors.⁵ Carbon-based solids are considered as the most promising candidates because of their high conductivity, low cost, and diverse availability.⁶ In addition, vast precursors including biomass,^{7,8} small organic molecules,^{9–11} metal–organic frameworks (MOFs),^{12–14} and porous organic polymers (POPs)^{15–17} facilitate the feasible preparation of carbon materials with different components and structures. According to previous reports, ultramicro-porosity

(pore size < 0.7 nm) is a desirable characteristic, which provides a favorable path for electrolyte penetration and transportation to realize an excellent electrochemical performance.¹⁸ However, the precursors usually suffer from the carbonization treatment at a high temperature (>600 °C) resulting in uncontrollable pore size.¹⁹ Therefore, fine-tuning microporosity in a narrow region of 0.5–0.7 nm is extremely difficult, and the relevant progress is scarce until now.

Porous aromatic frameworks (PAFs) are a kind of functional porous materials, which are known for their low density, large surface area, and superior chemical and thermal stabilities.²⁰ Diversified building monomers and stable covalent bonding patterns make them novel precursors for porous carbon materials for supercapacitor electrodes.^{21,22} Herein, a side chain (adjacent octyl groups) serving as a space-holder was grafted on the PAF skeleton (LNU-16) through Suzuki coupling reaction (Scheme 1a). The introduction of flexible chains facilitated the evolution of spherical configuration affording stacked cavities for ion storage and diffusion. Through high-temperature carbonization, the alkyl units decomposed and escaped from the solid framework, which provided extra space for the thermal-driven skeletal deformation to obtain ultramicropores (<0.7 nm). Based on the elaborate design, LNU-16-800 achieved outstanding performance with a capacitance of 294 F g⁻¹ at a current density of 0.5 A g⁻¹. The self-sacrificial

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Scheme 1 (a) Schematic synthesis route for LNU-16 by Suzuki coupling reaction. (b) Carbonization process of LNU-16, including chain escape (i) and structure engineering (ii), in which the purple sphere represents the PAF sample (LNU-16) with alkyl chains in the solid particle; the dark yellow sphere represents the carbonized LNU-16 under 500–600 °C treatment with alkyl chains decomposed from the particle; the brown sphere represents the carbonized LNU-16 under 700–900 °C treatment.

template route realized enriched ultramicropores in porous carbons *via* a simple step, which is more effective than other extensively investigated activation strategies such as physical activation (using steam and CO₂, *etc.*) and chemical activation (using KOH and NaOH, *etc.*).

2. Experimental

2.1 Materials

9,9-Dioctylfluorene-2,7-bis(boronic acid pinacol ester), 9,9-dimethylfluorene-2,7-bis(boronic acid pinacol ester), and 2,4,6-tris(4-bromophenyl)-1,3,5-triazine were purchased from J&K Chemicals. Tetrakis(triphenylphosphine)palladium was received from TCI. Nafion solution (5 wt%) was acquired from Sigma-Aldrich. Other materials were obtained from commercial suppliers and used without further purification.

2.2 Characterization

FTIR was performed using KBr pellets on a Shimadzu-Prestige 21 Fourier transform infrared spectrometer. Solid-state ¹³C-NMR spectra were measured on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz. TGA was performed using a

METTLER TOLEDO TGA/DSC 2 thermal analyzer under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. PXRD was carried out on a Bruker D8 QUEST diffractometer with Cu-K α radiation. XPS was performed on a K-Alpha XPS spectrometer (Thermo Fisher Scientific, MA, USA). Raman spectra were collected using a Renishaw inVia Raman microscope at 532 nm excitation. SEM analysis was performed on a SU8010 model scanning electron microscope with an accelerating voltage of 5 kV. TEM was performed on a JEM-2100 with an accelerating voltage of 200 kV. N₂ adsorption isotherms were obtained on a Micromeritics ASAP 2460 instrument. CHN element analysis was conducted using a PerkinElmer 2400 Series CHN Elemental Analyzer.

2.3 Synthesis of LNU-16

LNU-16 was synthesized *via* Suzuki coupling reaction (Scheme 1a). 9,9-Dioctylfluorene-2,7-bis(boronic acid pinacol ester) (531 mg, 0.8 mmol) and 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (303 mg, 0.5 mmol) were dissolved in 60 mL of *N,N'*-dimethylformamide (DMF) and then degassed by three freeze-pump-thaw cycles. Next, 5 mL of potassium carbonate (K₂CO₃, 2 M) and 40 mg (0.035 μ mol) of tetrakis(triphenylphosphine)palladium were quickly added into the system. After degassing *via* three freeze-pump-thaw cycles, the mixture was stirred at

130 °C for 48 h. Cooling down to room temperature, the residue was filtered and washed with tetrahydrofuran, distilled water, and acetone, respectively, to remove all the unreacted monomers and catalyst. Further purification of the product was carried out *via* Soxhlet extraction using tetrahydrofuran, dichloromethane, and methanol in turns for 72 h. The product was dried in vacuum for 10 h at 90 °C to get LNU-16 (483 mg, 91.3% yield).

2.4 Preparation of C-LNU-16s

The LNU-16 powder was heated at different temperatures (500, 600, 700, 800, and 900 °C) in a tubular furnace at the rate of 5 °C min⁻¹ and maintained for 2 h under a nitrogen gas flow (Scheme 1b). After cooling to room temperature, the resulting porous carbon materials (C-LNU-16s) were named as LNU-16-500, LNU-16-600, LNU-16-700, LNU-16-800, and LNU-16-900.

2.5 Electrochemistry measurement

The working electrode was fabricated by pressing the porous carbon materials (2 mg) into a mixture of deionized water (0.75 mL), ethanol (0.20 mL), and Nafion (50 μL, 5 wt%). After that, the mixture was dispersed by sonication for at least 30 min to obtain a homogeneous ink. Next, 8 μL ink was cast onto the surface of a mirror-polished glassy carbon (GC) electrode by using a microsyringe and dried at a temperature of 50 °C.²³ The prepared working electrode was evaluated on a CHI 660E (Chenhua, Shanghai) electrochemical workstation using 6 M KOH as the electrolyte.

Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrical impedance spectroscopy (EIS), and cycling stability of the carbon samples were conducted by employing a traditional three-electrode system with Ag/AgCl electrode and platinum wire as the reference electrode and counter electrode, respectively. The specific capacitance (C , F g⁻¹) of the carbon materials was calculated from the GCD curve using the following eqn (1):

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

where I (A) is the discharge current, Δt (s) represents discharge time, m (g) signifies the mass of the carbon materials, and ΔV (V) denotes the potential range.

For the two-electrode system, the specific capacitance (C_s , F g⁻¹), energy density (E , W h kg⁻¹) and power density (P , W kg⁻¹) were calculated using eqn (2)–(4):

$$C_s = \frac{4I \times \Delta t}{m \times \Delta V} \quad (2)$$

$$E = \frac{C_s \times (\Delta V)^2}{28.8} \quad (3)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (4)$$

where I (A) is the discharge current, ΔV (V) refers to the potential change within the discharge time Δt (s), and m (g) is the total mass of the materials.

3. Results and discussion

LNU-16 was prepared using the octyl-containing monomer *via* Suzuki cross-coupling reaction (Scheme 1). According to the Fourier transform infrared spectroscopy (FTIR) spectra (Fig. S1†), the C–Br stretching band located at 1064 cm⁻¹ is obviously weak. Meanwhile, the two peaks at 1417 cm⁻¹ (C–B) and 1351 cm⁻¹ (B–O) disappeared in comparison to the spectrum of the raw monomer, indicating the completion of the coupling reaction. Solid-state ¹³C NMR spectroscopy was used to determine the chemical structure of the PAF sample. As shown in Fig. S2,† the chemical shifts of –CH₃ and –CH₂– is centred at 22 and 30 ppm, respectively. The presence of aromatic carbons appears in the range of 120–150 ppm; the specific carbon atoms of each peak are distinguished by letters. The C peak at 140.7 ppm in the spectrum of LNU-16 confirms the successful phenyl–phenyl interaction.

As observed in Fig. S3,† LNU-16 possesses an amorphous structure determined by the powder X-ray diffraction (PXRD) pattern. Scanning electron microscopy (SEM) images show that LNU-16 has a well-defined spherical geometry and uniform particle size distribution of *ca.* 200 nm (Fig. 1a). For comparison sake, we used 9,9-dimethylfluorene-2,7-bis(boronic acid pinacol ester) to replace the alkyl-appended monomer in LNU-16 (Fig. S4†). The characterizations in Fig. S5 and S6† indicate the successful preparation of the non-chain modified PAF skeleton (LNU-17). In contrast, LNU-17 reveals a non-spherical morphology (Fig. S7†). This phenomenon is attributed to the high content of flexible chain that destroyed the planarity of the polymer backbone, which is in favour of a spherical morphology compared with twisted configurations.²⁴ Transmission electron microscopy (TEM) also confirms the amorphous structure of LNU-16; it clearly reveals a dense architecture of the PAF material (Fig. 1b).²⁵

LNU-16 could not be dissolved or decomposed in various solvents (DMF, ethanol, THF, CHCl₃, CHCl₂, acetone, *etc.*), which suggested its outstanding solvent stability. The thermal stability of LNU-16 was measured in a nitrogen atmosphere to study the thermal curing and carbonization process. As shown in thermogravimetric analysis (TGA) curves, there is *ca.* 4.5% weight loss before 350 °C, corresponding to the ring opening of the LNU-16 structure (Fig. 2a).²⁶ After that, the appended alkyl chains fracture in the range of 350–600 °C with a char yield higher than 35.5 wt% (Scheme 1b), which is basically identical with the theoretical amount (38.9%).²⁷ Finally, the weight decreases gradually with the thermal curing of aromatic rings.²⁸ During this period, azine segments produce nitrogen gas as a thermal decomposition product.²⁹ Furthermore, we performed the CHN element analysis (Table S1†) and X-ray photoelectron spectroscopy (XPS) to determine the content of nitrogen (Fig. S8†). As depicted in Fig. 2b by XPS calculations, the N content increases from 2.1% in parent LNU-16 to 3.6% in LNU-16-600, which is attributed to the decomposition of alkyl chains. Because of the production of nitrogen gas, the nitrogen amount decreases to 2.2% for LNU-16-900. All these values agree with the results obtained from TGA analysis.



Fig. 1 SEM (a) and TEM (b) images of LNU-16. SEM (c) and TEM (d) images of LNU-16-600. SEM (e) and TEM (f) images of LNU-16-800.

Finally, FTIR analysis was adopted to monitor the thermal transforming behaviour of the LNU-16 structure under thermal treatment as shown in Fig. 2c. The C–H (alkyl group) stretching vibration at 2854 cm^{-1} disappeared as the temperature increased from 500 to 600 °C, indicating the loss of alkyl chains. Meanwhile, the triazine moiety decomposed at 500–600 °C, proved by the vanishing of C=N and C–H (aromatic group) signals at 1500 and 2925 cm^{-1} , respectively. As the temperature increased to 700 °C, the intensity of C=N and C–H (aromatic group) peaks increased due to the regeneration of C and N doped aromatic ring.³⁰

The PXRD patterns show that the porous carbon materials are amorphous (Fig. S9†), and the characteristic peak of graphite has a trend of gradually moving right from 22° (2θ) for LNU-16s (500 and 600 °C) to 25° (2θ) for LNU-16s (700 and 800 °C). This phenomenon could be probably attributed to

that the graphitization of the PAF networks scales up as the temperature increased to 700–800 °C.³¹ Additionally, two distinct peaks at 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band) are observed for the carbonized LNU-16s in the Raman spectrum (Fig. S10†), which are assigned to crystal defects and in-plane vibrations of sp^2 hybridized carbons, respectively.¹⁸

The relative intensity of the D to G band (I_D/I_G) increased from 0.74 to 0.96 as the temperature increased from 600 to 900 °C, indicating the generation of more defects at higher activation temperatures (Scheme 1b).³² On the basis of the spherical particles, the porous carbon materials demonstrate that they retain the original morphologies as observed from the SEM images (Fig. 1 and S11†). Accordingly, the loss of flexible chains and structural engineering processes can be observed from the TEM images. As shown in Fig. 1d and f, the worm-like channels were gradually formed along with the



Fig. 2 (a) TGA curve in nitrogen environment for LNU-16. (b) Nitrogen elemental comparison for LNU-16 and carbonized PAF materials. (c) FTIR spectra for LNU-16 and carbonized PAF materials. (d) N_2 adsorption (filled symbols)–desorption (empty symbols) isotherms for LNU-16. Inset: the pore size distribution curve calculated by the NL-DFT method for LNU-16. (e) N_2 adsorption (filled symbols)–desorption (empty symbols) isotherms for carbonized PAF materials. (f) Pore size distribution curves by the NL-DFT method for carbonized PAF materials.

increase of temperature from 600 to 800 °C. The smooth carbon spheres together with ultra-micropores are favourable for the diffusion and transfer of electrolytes.³³

According to the nitrogen adsorption–desorption analysis (Fig. 2d), LNU-16 shows almost no gas sorption at a relatively low pressure, indicating that its pore channels are occupied by the alkyl groups. The Brunauer–Emmett–Teller (BET) surface area of LNU-16 is $21.64 \text{ m}^2 \text{ g}^{-1}$ and the total pore volume is $0.026 \text{ cm}^3 \text{ g}^{-1}$. Unlike the parent PAF structure (LNU-16), the porous carbons (C-LNU-16s) show type I isotherm with a high gas uptake at low relative pressures, which suggests the gradual formation of ultramicropores in these carbon materials (Fig. 2e).³⁴ As observed in Fig. 2f, the treated LNU-16 samples under 600 °C show the emerging pore cavity in the range of 0.5–1 nm based on the NL-DFT model. This is due to the escape of octyl groups from PAF solid to obtain newly formed cavities. As for LNU-16-700, the alkyl chain is almost completely removed from the dense architecture of LNU-16, and porous channels are obtained with a size similar to the kinetic diameter of adjacent octyl units (0.8–1 nm). With the increase of temperature (LNU-16-800 and LNU-16-900), the newly formed micropores provide the space for structural engineering, which leads to the further transformation of the porous skeleton to shrink the pore channels into ultramicropores (<0.7 nm) of 0.56–0.64 nm (Table 1).^{35,36} It is worth mentioning that LNU-16-800 has the largest surface area and micropore volume, which may provide more accessible space for electrolytes, thus facilitating the enhancement of capacitance.³³

Based on the above characterizations, the series of carbonized PAF materials possess all the requirements to become ideal electrode materials. The electrochemical properties of the LNU-16s 700–900 were systematically investigated in a 6 M KOH aqueous electrolyte. Electrochemical impedance spectroscopy (EIS) was performed with the frequency of 10^{-2} to 10^5 Hz in order to examine the ion diffusion feature and the conductivity of LNU-16s 700–900. As illustrated in Fig. 3a, the Nyquist plots reveal that LNU-16-800 endows the electrode with lower solution resistance ($R_s = 2.92 \Omega$), whereas higher resistances were observed for LNU-16-700 ($R_s = 3.83 \Omega$) and LNU-16-900 ($R_s = 3.84 \Omega$). The lower solution resistance of LNU-16-800 is beneficial for superior capacitive performance.³⁷ Correspondingly, the diameter of the semicircle in the high frequency of LNU-16-800 is smaller than those of LNU-16-700 and LNU-16-900, suggesting a smaller charge-transfer resistance. The x -intercept of the Nyquist plot corresponds to the equivalent series resistance (ESR); the vertical line of LNU-16-800 is more parallel to the y -axis specially, which indicates a very low equivalent series resistance of this supercapacitor electrode.²²

The cyclic voltammogram (CV) curves of carbon materials at a scan rate of 10 mV s^{-1} display relatively quasi-rectangular shapes (Fig. 3b), which is the typical characteristic of electrical double layer (EDLC) behaviour. Since LNU-16-800 shows a larger current density area, it can initially predict a higher specific capacitance for LNU-16-800. The CV curves of LNU-16s 700–900 maintain the basic shape without obvious redox peak from 2 to 100 mV s^{-1} (Fig. 3c and S12†), indicating an excellent

Table 1 Porosity parameters of carbonized LNU-16s

	S_{BET}^a	V_{total}^b	V_{Micro}^c	S_{Micro}^c	$P_{\text{ultramicro}}^d$	$P_{\text{supermicro}}^e$
LNU-16-500	288.63	0.21	0.082	179.81	0.64	1.12
LNU-16-600	513.75	0.40	0.182	394.52	0.57	1.18
LNU-16-700	422.10	0.33	0.160	333.21	0.56	1.00
LNU-16-800	515.86	0.34	0.204	456.25	0.56	—
LNU-16-900	509.00	0.41	0.198	403.70	0.56	—

^a Specific surface area determined by the BET method. ^b Total pore volume calculated by the DFT method. ^c Micropore area and volume calculated by the *t*-plot method. ^d Pore size of ultramicropores. ^e Pore size of supermicropores.



Fig. 3 (a) Nyquist plots for LNU-16s 700–900 in the frequency range of 10^{-2} to 10^5 Hz. (b) CV curves for LNU-16s 700–900 at a scan rate of 10 mV s^{-1} . (c) CV curves for LNU-16-800 at different scan rates. (d) GCD curves for LNU-16s 700–900 at a current density of 1 A g^{-1} . (e) GCD curves for LNU-16-800 at different current densities. (f) The curves of specific capacitances against various current densities for LNU-16s 700–900.

capacitive characteristic with a rapid ion spread and charge transportation.²²

Galvanostatic charge–discharge (GCD) curves at 1 A g^{-1} for LNU-16-based porous carbons are shown in Fig. 3d. The curves depict a typical triangular shape between -1 and 0 V , indicating an outstanding electrochemical capacitive behavior.³⁸ As expected, LNU-16-800 displays a longer discharge time at 1 A g^{-1} . The GCD curves of LNU-16s 700–900 are listed in Fig. 3e and S13† at various current densities, and almost no obvious voltage drop could be observed even at a high current density of 10 A g^{-1} . The excellent symmetry of GCD curves is attributed to the good electrical conductivity and high coulombic efficiency of these carbon materials.^{8,39} As for the decrease of specific capacitance at a higher current density, it is common in porous carbon-based electrode materials as the electrolyte ions could not easily diffuse into the micropores at a high current density (Fig. 3f).³² The specific capacitance of LNU-16-800 was calculated to be 294 F g^{-1} at 0.5 A g^{-1} , which is comparable with or better than the previous reports focused on the construction of

micropores and ultramicropores (Table S2†), including self-template strategy (206 F g^{-1} at 1 A g^{-1}),⁸ carbonization of covalent benzoxazine framework (185 F g^{-1} at 1 A g^{-1}),²⁶ carbonization of PAF-1 (146 F g^{-1} at 1 A g^{-1}),⁴⁰ template-assisted strategy (268 F g^{-1} at 0.25 A g^{-1}),⁴¹ and carbonization of nanoparticles (206 F g^{-1} at 1 A g^{-1}).⁴² The superior capacitance performance of the carbonized LNU-16 is attributed to the abundant ultramicroporosity coupled with the spherical morphology, enabling easier accessibility of electrolytes to the electrode surface. Furthermore, the performance of LNU-16-800 is also comparable with the best performing materials such as carbon spheres,^{43–45} hierarchical porous carbon,⁴⁶ carbon nanotubes,^{47,48} N-doped porous carbons,⁴⁹ COF-based materials,⁵⁰ CMP-based materials,^{51,52} and MOF-based materials (Table S3†).^{53,54}

In order to confirm the long-term cyclic stability of the LNU-16-800 material, galvanostatic charge–discharge tests were investigated at a current density of 10 A g^{-1} (Fig. 4a). The specific capacitance of LNU-16-800 slowly increased up to 171 F g^{-1} along with the charge/discharge cycles. Interestingly, the



Fig. 4 (a) Cycling performance for LNU-16-800 over 10 000 cycles at the current of 10 A g⁻¹. (b) Ragone plot for LNU-16-800 and other reported energy storage devices.

maximum capacitance retention of 120% was acquired after 10 000 cycles, which means the electrochemical active sites get activated and participated in stable electrochemical reactions.⁵² On evaluating the energy density (E) and power density (P) using a two-electrode system, LNU-16-800 demonstrated an energy density of 10.2 W h kg⁻¹ at the power density of 50.8 W kg⁻¹; these characteristics are competitive among the previous reports under similar conditions (Fig. 4b), for instance, carbon spheres,^{22,56} porous carbon,^{31,46,57} hollow carbon microspheres,⁴⁹ COF-based materials,⁵⁰ porous carbon prepared by activation strategies,^{59,55,58} self-template strategy,⁶⁰ and biomass-derived microporous carbon.^{61,62} The results illustrate that the self-sacrificial template method is a simple and promising strategy for fabricating ultramicroporous N-doped carbon to enhance the electrochemical performance of supercapacitors.

4. Conclusions

In summary, a facile and effective method, self-sacrificial template approach, has been investigated to prepare novel PAF-based carbon materials with ultramicroporosity. During the process, the introduced alkyl chains regulate the morphology of PAF powder into smooth spheres. After the carbonization treatment, the space holders (octyl groups) escape from the dense structure and leave the pore channels for further structural

engineering, producing a rational ultramicroporous structure. The well-prepared pore architecture together with ideal spherical morphology provides optimized pathways to serve as ion-pathways for rapid diffusion of electrolyte ions. Based on these results, our strategy is more effective than all other methods for the preparation of ultramicropores. The self-sacrificial template method will open a new avenue for ultramicroporous carbon materials, thus providing possibilities to develop new electrode materials in the field of supercapacitors.

Conflicts of interest

There are no conflicts to declare.

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