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Abstract

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Controlled synthesis of mesoporous nitrogen-doped carbons with highly ordered two-dimensional hexagonal mesostructures and their chemical activation†

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Ordered mesoporous nitrogen-doped carbon (OMNC) materials are considered as the most promising material for supercapacitors. In this study, a highly ordered two-dimensional (2D) hexagonal mesostructured polymer was synthesized through a facile assembly of triblock polymer micelles and phenol-melamine/formaldehyde resin via an organic–organic assembly process in aqueous solution. After calcination, the novel OMNC materials with 2D hexagonal mesostructures were obtained. By further KOH activation, the surface area and the porosity of the OMNC significantly improved, and the internal mesoporous structures were maintained. The activated OMNC-800A displayed a specific capacitance as high as 475.75 F g^{−1} at 0.5 A g^{−1} with an outstanding cycling stability (over 100% capacitance retention during 2000 cycling tests at 100 mV s^{−1}). These results confirm that the tubular mesochannels inside the OMNC are very beneficial in providing an accessible path for diffusion of the electrolyte, thereby improving the specific capacitance of OMNC at a high current density.

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1. Introduction

Mesoporous carbon materials show several exceptional properties including ultrahigh surface areas, large pore volumes,

controllable mesoporous structures, *etc.*^{1,2} These materials are ideal candidates for a myriad of applications, particularly electrochemical energy conversion and storage.^{3–5} To date, hard- and soft-templating approaches have been employed for the preparation of ordered mesoporous (OMC) carbon materials with controlled morphology, uniform pore structures and narrow pore size distribution. Hard-templating approaches including mesoporous silica have been utilized for the synthesis of mesoporous carbon materials.^{6–8} However, the hard-templating approach is a multistep process (*i.e.*, preparation of ordered templates, replication of mesopores with appropriate carbon precursors, carbonization, and removal of the template matrix). In this case, the rational design and control of templates are the key factors for producing high-quality mesoporous materials which are slightly complex, time and cost consuming, and unfavorable for mass production. In contrast, the soft-templating method is a straightforward approach which is dependent on the self-assembly of the organic compounds and block copolymers into ordered mesostructured composites in a oriented manner through a chemical interaction.^{9–13} Interestingly, the morphology, porosity, and structure could be tuned by controlling the synthetic conditions, such as the concentration of the surfactant, pH, and carbonization temperature. The morphological control will endow the product with an excellent chemical activity,

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mechanical stability, good electrical conductivity, and high surface area, which have been considered as the essential requirements for electrode materials used in energy storage applications.^{14,15}

Supercapacitors have received considerable attention in customer electronics, communication, and transportation systems because of their superior power density and long cycling durability.^{16,17} Research efforts are still directed toward increasing the power density and extending the long-term durability of electrodes to fulfill the requirements of high power delivery/uptake in portable electronics and other equipment with high power demands.^{18,19} Controlling pore size distribution is another crucial factor for carbon electrodes to boost high power density by exposing the accessible surface and providing a diffusion path for electrolytes.^{20–23} Besides, it was also proved that not only the high surface area but also other parameters, such as nitrogen doping²⁴ and carbon particle size,²⁵ are crucial for improving the specific capacitance and the rate performance of carbon electrodes in supercapacitors. Therefore, it is expected that the fabrication of ordered mesoporous nitrogen-doped carbon (OMNC) may integrate the advantages of OMC with nitrogen doping. We can expect that the presence of tubular mesochannels is also beneficial to exposing the accessible surface area and accelerating the diffusion of electrolytes. However, synthesizing OMNCs with 2D hexagonal mesostructures still remains a challenge due to the complications in optimizing the synthetic conditions.^{26–31}

In this study, a highly ordered two-dimensional (2D) hexagonal mesostructured polymer was synthesized through a facile assembly of triblock polymer micelles and phenol-melamine/formaldehyde resin *via* an organic–organic assembly process in aqueous solution. The symmetric triblock polymer Pluronic P123 was used as a mesopore-direct agent, and phenol/formaldehyde and melamine/formaldehyde resin were used as carbon and nitrogen sources, respectively. After calcination, the as-prepared OMNC possessed uniformly sized mesopores and plentiful tubular mesochannels. With further KOH activation at high temperatures, the morphology and ordered mesopores of OMNC were still maintained, and they also showed an ultrahigh surface area (over 2400 m² g^{−1}) mainly by creating abundant micropores. As a supercapacitor electrode, the activated OMNC showed outstanding specific capacitance as high as 475.75 F g^{−1} at 0.5 A g^{−1} and remarkable long-term stability.

2. Experimental section

2.1. Chemicals

Pluronic P123 (PEG-PPG-PEG), melamine, and 5.0 wt% Nafion perfluorinated resin solution were purchased from Sigma-Aldrich. Phenol, formaldehyde (37 wt%), 0.1 M sodium hydroxide, and 1 M H₂SO₄ were purchased from Nacalai Tesque, Inc. All the chemicals were of analytical grade and used as received.

2.2. Preparation of ordered mesoporous nitrogen-doped carbon (OMNC)

Firstly, the mesostructured polymer was prepared *via* an organic–organic assembly process in aqueous solution with the assistance of the triblock copolymer Pluronic P123. Phenol-melamine/formaldehyde resin (P-M/F) was added as carbon and nitrogen sources. Typically, 0.28 g of phenol and 0.19 g of melamine were dissolved in 1.5 mL of formaldehyde aqueous solution (37 wt%) under stirring at 60 °C, leading to a colorless transparent solution after 5 min. Then, 2.0 mL 0.1 M NaOH solution was added into the above clear solution and stirred at 70 °C for 30 min. After this, 10.0 mL P123 aqueous solution (containing 0.325 g of P123) was added and the solution was stirred at 65 °C for 2 h. Subsequently, 25.0 mL of distilled water was added to the mixture and the diluted solution was further kept at 65 °C for another 10 h under mild stirring, resulting in a dark-red solution. After that, 10.0 mL of the obtained dark-red solution was transferred in a Teflon liner under vigorous stirring. The pH value was adjusted to *ca.* 9.3 by adding an appropriate volume of 0.1 M NaOH solution. The Teflon liners were transferred into autoclaves (100 mL) for a hydrothermal reaction at 130 °C for 20 h with a ramping rate of 1 °C min^{−1}. The obtained precipitate was collected by centrifugation (14 000 rpm for 5 min) and washed with water and ethanol three times. After drying at 60 °C, the mesostructured polymers were obtained. The synthetic conditions (*e.g.*, concentration of P123 and pH) for controlling the morphology of the precursor were carefully investigated and the corresponding products were denoted as N/C-*x* (*x* = 1, 2, 3, 4, and 5). The detailed synthesis parameters are listed in Table 1. The as-made precursor was carbonized at controlled temperatures for 4 h under a N₂ atmosphere. The ramping rate of the calcination process was 5 °C min^{−1}. The pre-carbonized ordered mesoporous nitrogen-doped carbons were denoted as OMNC-*T*, where *T* represents the calcination temperatures (700, 800, and 900 °C).

2.3. KOH activation of OMNC-*T*

25.0 mg of OMNC-*T* was mixed with 100.0 mg potassium hydroxide (KOH). Then, the mixture was dispersed in 5 mL of deionized water under sonication for 30 min. The slurry was dried at 100 °C overnight, following by thermal treatment at 800 °C for 2 h under flowing N₂ with a ramping rate of 5 °C min^{−1}. After cooling to room temperature, the resulting powder was washed with deionized water to remove KOH completely. Finally, the activated OMNC-*T* was dried in an oven at 80 °C and labeled as OMNC-TA.

Table 1 Different preparation conditions with changing P123 concentrations or pH values

Samples	Concentration of P123 (mg mL ^{−1})	pH values
N/C-1	32.5	8.5
N/C-2	32.5	9.3
N/C-3	32.5	10.0
N/C-4	10.0	9.3
N/C-5	100.0	9.3

2.4. Characterization

The morphology of the samples was characterized by using a field emission scanning electron microscope (SEM, HITACHI SU-8230) operating at 5.0 kV. A transmission electron microscope (TEM, JEOL JEM-2100F) operated at 200 kV was employed to investigate the inner mesoporous structure. Small angle X-ray scattering (Rigaku NANO Viewer; Cu K α radiation; 40 kV, 30 mA) equipped with a camera length of 700 mm was used to evaluate the pore-to-pore distance. Wide-angle X-ray diffraction (XRD) patterns were acquired with a Rigaku Rint 2000 X-ray diffractometer using monochromated Cu K α radiation (40 kV, 40 mA) at a scanning rate of 1° min⁻¹. Nitrogen adsorption-desorption isotherms were obtained using a BELSORP-mini (Bel Japan, Inc.) at 77 K. The specific surface area (SSA) was evaluated by the multipoint Brunauer-Emmett-Teller (BET) method at a relative pressure from 0.05 to 0.3 based on the adsorption data. The chemical state of nitrogen was investigated using X-ray photoelectron spectroscopy (PHI Quantera SXM) with Al K α radiation (20 kV, 5 mA). The binding energy shift was calibrated using the C1 s level at 284.5 eV.

2.5. Electrochemical measurements

The as-prepared OMNC-*T* and OMNC-800A were ground before preparing inks. In a typical experiment, 2.0 mg of sample was dispersed in 400 μ L of 1:2 (v/v) isopropanol/water mixed solvent (containing 20 μ L of 5.0 wt% Nafion solution) under sonication for at least 30 min to form a homogeneous ink. After that, 200 μ L of the suspension was dropped onto flexible graphite paper (thickness: 1 mm) with an area of 1 $\times$ 1 cm² and dried at 60 °C. The mass loading was 1.0 mg cm⁻² and the thickness of the electrode film was found to be around 15–25 μ m. In addition, we choose flexible graphite paper as the current collector because of its excellent electrical conductivity as well as its negligible capacitive performance (usually below 1 F g⁻¹), which would contribute little to the total capacitance of the prepared working electrode. All electrochemical measurements were carried out on a CHI 660E instrument. In a three-electrode system, the electrochemical performances of the as-made OMNC-*T* and OMNC-800A electrodes were investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) in 1 M H₂SO₄, with a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The specific capacitance of the as-made electrodes was calculated from the GCD curves. The test of long-term stability for OMNC-800A was conducted by cycling between 0.0 and 0.8 V *vs.* Ag/AgCl in 1 M H₂SO₄ at a scan rate of 100 mV s⁻¹.

In general, the gravimetric specific capacitance (C_g , F g⁻¹) was calculated using the following equation:

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

where I is the discharge current (A), t is the discharge time (s), m is the mass of the active material (g), and ΔV is the potential change during the discharge process (V).

3. Results and discussion

Fig. 1 shows the SEM images of the as-prepared polymer particles with different P123 concentrations and pH values. The optimized polymer particles show a hexagonal prism-like structure with a size distribution of 200–400 nm (Fig. 1b). Thus, to gain deep understanding of morphology control, the role of P123 concentration and pH was investigated systematically (Table 1). The optimized mesostructured polymer (N/C-2) was obtained at a pH value of 9.3 with a P123 concentration of 32.5 mg mL⁻¹, while spherical particles (N/C-1, pH = 8.5) and irregular nanoparticles (N/C-3, pH = 10.0) were obtained (Fig. 1a–c). This is more likely related to the polymerization rate of low molecular phenol-melamine/formaldehyde resin (P-M/F), determined by the concentration of the NaOH catalyst. Fig. 1d and e display the morphology changes derived from the altered concentration of P123 with the optimized pH value of 9.3. As can be clearly seen, the morphology of the polymer particles was changed from spherical (N/C-4) to hexagonal prism (N/C-2) and finally to irregular cross-linked particles (N/C-5) with the increase of P123 concentration. As evidenced by small angle X-ray scattering (SAXS) analysis (Fig. S1†), the SAXS pattern of the optimized polymer particles (N/C-2) showed an obvious peak, while a less ordered mesostructure of polymer particles was confirmed for non-optimized polymers (*i.e.*, N/C-1, -3, -4, and -5).

SEM and TEM images in Fig. 2a–c, S2a, b, and S3a, b,† show the calcined N/C-2 samples at different temperatures. Regardless of the calcination temperature, the morphology and mesostructures are well maintained, indicating remarkable thermal stability of the carbon framework of OMNC. After the removal of P123 micelles during carbonization, the TEM images reveal the ordered mesopores for OMNC-700, OMNC-800, and OMNC-900 with a size of *ca.* 2.7, 3.6, and 3.0 nm (Fig. 2b, c, S2b, and S3b†), respectively. From the TEM observation of individual particles (Fig. S4†), it was clearly seen that the tubular mesochannels are running in the same direction within one particle, which can act as diffusion pathways for the electrolytes. As seen in Fig. 2d–f, S2c, d, and S3c, d,† the original morphology and mesostructures were maintained even after KOH activation at high temperature. The retention of 2D hexagonal mesostructures was also confirmed by SAXS patterns (Fig. 3a and S5a†), further demonstrating the excellent structural stability of carbon walls between mesopores. Notably, it is ordinary to achieve the irregularly shaped ordered mesoporous carbon (OMC) with 2D hexagonal symmetry,^{31–33} while the hexagonal ordered mesoporous nitrogen-doped carbon (OMNC) particles have been rarely reported.

The SAXS patterns in Fig. 3a and S5a† show three resolved peaks which can be indexed to (10), (11) and (20) reflections. Compared with N/C-2 (Fig. 1b), the (10) peaks are shifted to higher values because of the polycondensation of P-M/F resin and the shrinkage of the carbon framework after calcination. As listed in Table 2, the d_{10} spacing reduces from 12.17 nm (N/C-2) to 8.85 nm (OMNC-700), 8.44 nm (OMNC-800), and 8.39 nm (OMNC-900) with increasing calcination temperature from

Fig. 1 (a–c) SEM images of the as prepared polymer particles with P123 concentration of 32.5 mg mL^{-1} at different pH values [(a) N/C-1 (pH = 8.5), (b) N/C-2 (pH = 9.3) and (c) N/C-3 (pH = 10.0)]. (d and e) SEM images of the as prepared polymer particles using different concentrations of P123 at a pH value of 9.3 [(d) N/C-4 (10.0 mg mL^{-1}) and (e) N/C-5 (100.0 mg mL^{-1})].

700 to 900 °C. After activation with KOH, as seen in Fig. 3a and S5a,† SAXS patterns show reduced intensity of activated samples, especially for OMNC-900, indicating the deterioration of the ordered mesoporous structure due to the etching of carbon walls and the new generation of micropores.^{32,33}

The wide-angle X-ray diffraction (XRD) patterns of all samples show two characteristic graphitic peaks located at

around 23° and 44° which can be assigned to (002) and (101) planes (Fig. 3b and S5b†), respectively. After KOH activation, the peak of the (002) plane disappeared except for OMNC-900A because OMNC-900 pre-carbonized at a higher temperature was more stable than OMNC-700 and OMNC-800 during activation. This variation should be ascribed to the etching reaction between the carbon framework and KOH

Fig. 2 SEM, TEM, and HAADF-STEM images of representative samples: (a–c) OMNC-800 carbonized at 800 °C; (d–f) corresponding activated product OMNC-800A.

which consumed the carbon skeleton and created more pores.^{34,35}

High resolution X-ray photoelectron spectroscopy (XPS) was conducted for the representative OMNC-800 and activated OMNC-800A (Fig. 3c) to characterize the chemical state of

nitrogen. The N 1s XPS spectra of OMNC-800 and OMNC-800A were deconvoluted into four peaks at 398.2 eV (pyridinic N), 399.5 eV (pyrrolic N), 400.9 eV (graphitic N), and 403.2 eV (oxidized N).^{36,37} The N content of 6.5 at% (OMNC-800) was decreased to 0.9 at% (OMNC-800A) after KOH activation due to

Fig. 3 (a) SAXS patterns, (b) XRD patterns, (c) high-resolution N 1s XPS spectra, and (d) N₂ adsorption–desorption isotherms of OMNC-800 and OMNC-800A.

Table 2 Physicochemical properties of OMNC-*T* and OMNC-*TA* (*T* = 700, 800, 900)

Sample	d_{10} (nm)	Specific surface area (m ² g ^{−1})	Pore volume (cm ³ g ^{−1})
N/C-2	12.17	—	—
OMNC-700	8.85	696	0.37
OMNC-800	8.44	840	0.49
OMNC-900	8.39	893	0.45
OMNC-700A	8.57	1790	0.89
OMNC-800A	8.41	2450	1.34
OMNC-900A	8.14	1630	0.93

partial replacement of nitrogen by oxygen through the activation reaction.³⁸ The relative content of all N species in OMNC-800 and OMNC-800A was estimated by XPS analysis and is summarized in Fig. S6.† After KOH activation, the percentage of pyridinic N dropped from 29.43% for OMNC-800 to 4.65% for OMNC-800A. In contrast, the percentage of graphitic-N increased from 49.60% for OMNC-800 to 53.96% for OMNC-800A. These findings are consistent with the fact

that graphitic N is more stable than pyridinic N.³⁹ In general, pyridinic N and graphitic N in carbons are regarded as electro-active sites, which would benefit the enhancement of electrical conductivity as well as capacitances.^{40,41}

Based on the analysis of N₂ adsorption–desorption isotherms (Fig. 3d and S5c†), the increase of the calcination temperature from 700 to 800 and 900 °C led to the gradual increase in the specific surface area (SSA) from 696 to 840 and 893 m² g^{−1}, respectively. The KOH activation process caused a significant enhancement of the SSA for all activated samples, as shown in Table 2. The much higher N₂ uptake at a low relative pressure ($P/P_0 < 0.1$) for activated products (OMNC-*TA*) can be clearly observed, which indicates the formation of tremendous micropores after activation. The SSA of OMNC-800A is obviously higher than that of other activated samples, reaching up to 2450 m² g^{−1}. This was attributed to the highest pore volume of OMNC-800 which was beneficial to the deep impregnation of molten KOH. In addition, as mentioned above, OMNC-900 calcined at high temperature was more difficult to activate deeply by KOH.

Considering the unique structural advantages of OMNC-*T*, including well-dispersed particles, uniformly sized mesopores, tubular mesochannels, and high surface area, it is expected to be a promising electrode material for practical supercapacitors. To show the superiority of OMNC-800A, the electrochemical performances of OMNC-*T* and OMNC-800A were investigated in a three-electrode system using 1 M H₂SO₄ as the electrolyte. CV curves shown in Fig. 4a indicate that all samples display rectangle-like curves, revealing the typical electrical double layer capacitive properties of all samples. Remarkably, OMNC-800 exhibited a higher CV area than OMNC-700 and OMNC-900, suggesting that OMNC-800 has a better capacitive property compared to OMNC-700 and OMNC-900. In addition, after activation with KOH, the obtained OMNC-800A showed an improved capacitive performance compared to pristine OMNC-800. The specific capacitances at 0.5 A g⁻¹ (denoted as $C_{0.5}$) were calcu-

lated by GCD curves (Fig. 4b) for all samples (OMNC-*T* and OMNC-800A). The corresponding values of $C_{0.5}$ are 196.81 (OMNC-700), 332.12 (OMNC-800), 314.56 (OMNC-900), and 475.75 F g⁻¹ (OMNC-800A). Obviously, OMNC-800A displayed the highest specific capacitance of 475.75 F g⁻¹. To the best of our knowledge, this value is also higher than those for all the reported N-doped carbon values measured in an aqueous electrolyte utilizing a three-electrode system (Table S1†). In addition, the GCD plots shown in Fig. 4b are generally symmetric, which is indicative of high capacitive reversibility and very low internal resistance of all samples.

Fig. 4c shows the specific capacitances of OMNC-*T* and OMNC-800A calculated based on the discharge curves at various current densities from 0.5 to 10 A g⁻¹. As expected, the capacitance values of OMNC-800A surpass those of non-activated samples at any current density. In addition, even at a relatively high current density of 10 A g⁻¹, the capacitance

Fig. 4 (a) CV curves at 5 mV s⁻¹ scan rate, (b) galvanostatic charge-discharge curves at a current density of 0.5 A g⁻¹, and (c) specific capacitances at different current densities for OMNC-*T* (*T* = 700, 800, 900) and OMNC-800A; (d) cycling performance of OMNC-800A at 100 mV s⁻¹.

value of OMNC-800A as high as 325 F g^{-1} (Fig. S7†), displaying a remarkable rate capacitance retention (68%). Such excellent capacitance retention is an indication for quick charge propagation capability and easy ion transport within the OMNC-800A electrode material. To further demonstrate the superiority of OMNC-800A, the long-term stability was investigated by the CV measurement at 100 mV s^{-1} (Fig. 4d and S8†). Remarkably, the capacitance for the first 2000 cycles gradually increased until capacitance retention reached 113%, possibly due to the activation process of the OMNC-800A electrode by improved wetting of the electrolyte deep inside the mesochannels of the material. After 10 000 cycles, it retained 90% of its initial capacitance value, indicating a good electrode stability.

The above results indicate that OMNC-800A is a promising carbon material for supercapacitors. The superior capacitive performance can be ascribed to the following reasons: (i) OMNC-800A exhibited an ultrahigh specific surface area and a large pore volume ($2450 \text{ m}^2 \text{ g}^{-1}$ and $1.34 \text{ cm}^3 \text{ g}^{-1}$). As is well known, the high specific surface area and large pore volume of porous carbons usually result in high electrochemical double layer capacitance.^{42,43} (ii) OMNC-800A exhibited a novel hierarchically porous structure with plentiful mesochannels, not only guaranteeing the electrode wetting by the electrolyte, but also help to accelerate the ion transport.

4. Conclusion

In this study, we demonstrated the preparation of mesostructured polymer particles by a soft-templating approach using a P123 triblock copolymer. Phenol-melamine/formaldehyde resin was used as the carbon precursor and nitrogen source. After carbonization, OMNC materials with 2D hexagonal mesostructures were obtained. The further KOH-activated OMNC maintained the original 2D hexagonal mesostructures. Activated OMNC-800A featured a high specific surface area ($2450 \text{ m}^2 \text{ g}^{-1}$) and revealed an outstanding gravimetric specific capacitance of 475.75 F g^{-1} at a current density of 0.5 A g^{-1} and excellent stability with high capacitance retention in a three-electrode system. Moreover, the salient features of the synthetic approach developed in this study are simplicity, environmental friendliness, and reliability, which are beneficial to mass production for practical application in supercapacitors.

Conflicts of interest

There are no conflicts to declare.

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