



Short communication

Preparation of ordered mesoporous carbon nanpipes with controlled nitrogen species for application in electrical double-layer capacitors

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ARTICLE INFO

Article history:

Received 14 July 2009

Received in revised form 26 August 2009

Accepted 12 September 2009

Available online 30 October 2009

Keywords:

Nitrogen functionalization

Nitrogen state

Mesoporous carbon

Carbonization temperature

Capacitor

ABSTRACT

Nitrogen-doped mesoporous carbon nanpipes with various nitrogen states are prepared by controlling the carbonization temperature. Nitrogen adsorption–desorption and transmission electron microscopy (TEM) analyses reveal that the optimum carbonization temperature is 1123 K. A carbonization temperature below 1073 K is insufficient to form a mesoporous carbon framework, while collapse of the carbon structure is observed above 1173 K. X-ray photoelectron spectroscopy measurements clearly show that nitrogen species are chemically transformed into pyrrolic and quaternary state species with higher binding energies. In cyclic voltammetry measurements, polar species of quaternary nitrogen on a carbon surface show a positive effect to enhance the capacitance via an increase in hydrophilicity and wettability of carbon by the electrolyte.

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1. Introduction

The physical and chemical properties of carbon materials are important factors in the design of electrical double-layer capacitors (EDLCs) [1–9]. It is well known that the physical properties of carbon materials, including surface area, pore volume and pore size, are closely related to the capacitance of these materials [1–5]. Ordered mesoporous carbon materials (OMCs) have attracted much attention due to their unique properties, such as high surface area, large pore volume, narrow pore-size distribution, and uniform pore structure [5,10–12]. These unique physical properties make OMCs well suited as potential candidate materials for EDLCs.

Hard template and soft template methods are representative methods to prepare OMCs [13]. The former method uses silica, aluminosilicate or alumina, for the formation of a porous structure of carbon as the replica of a hard template. This method involves (1) the preparation step of hard template; (2) infiltration of carbon precursor into the template; (3) polymerization and carbonization; (4) removal of the hard template [10,13,14]. The soft template method for the preparation of OMCs uses amphiphilic molecules as structure derivatives and carbon precursors [15,16]. The advantages of

this method are no use of a hard template and simple synthetic steps.

Rod-type OMCs like CMK-3 and tube-type OMCs like CMK-5 are well-known mesoporous carbon materials [10,14]. Tube-type carbons have a bimodal pore structure, and additional pores offer certain advantages for EDLC application through the formation of micropores and mesopores.

Among the various chemical properties, the functionality of the carbon surface affects the capacitance via a pseudocapacitance effect [3,6,8,9,17]. In recent decades, various functionalization techniques for the carbon surface have been investigated by many researchers [3,6,8,9,18,19]. It is known that nitrogen functionality is effective in increasing the capacitance of carbon material [8,9,20]. Nitrogen on the carbon surface generally exists as pyridinic, pyrrolic, quaternary, and oxidized states [8,9]. The nitrogen state may affect the capacitance of carbon material. Therefore, an effective method for controlling the nitrogen state (nitrogen functionality) is required.

A well-known method for functionalizing OMCs with nitrogen functionality involves the use of acid and heat in the presence of nitrogen-containing materials. In this method, however, the pore structures of OMCs can be destroyed, leading to the formation of non-uniformly functionalized surfaces [19–21]. In addition, this method is not appropriate for preparing tube-type OMCs because these have weaker pore structures than rod-type OMCs [10,22]. Another method for functionalizing OMCs involves the use of

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nitrogen-containing carbon precursors such as poly-pyrrole, poly-acrylonitrile, quinoline, and related materials [8,9,23].

In this study, carbon nanopipes with ordered mesoporous structure are prepared for application in EDLCs. Quinoline is used as a nitrogen-containing carbon precursor, with the aim of functionalizing the OMC. The nitrogen state of the carbon surface is controlled by changing the carbonization temperature. The effect of the nitrogen state on the physicochemical property and EDLC performance of mesoporous carbon material is investigated.

2. Experimental

Ordered mesoporous carbon nanopipes (OMCNs) with nitrogen functionality were prepared by a hard templating method using a mesoporous aluminosilicate template (Al-SBA-15). Al-SBA-15 was prepared according to the method described elsewhere [10]. SBA-15 was impregnated with an aqueous solution of AlCl_3 ($\text{Si}/\text{Al}=20$). After drying the sample, it was calcinated at 823 K for 4 h to yield Al-SBA-15. Al-SBA-15 (1 g) was mixed with quinoline (1 mL) for the preparation of OMCN with nitrogen functionality. The mixed sample was introduced into an autoclave under an air atmosphere and heated to 523 K at a ramping rate of 1 K min^{-1} . The sample was then maintained at 523 K for 6 h. The resulting brown powder was treated in a fused-quartz tube at 473 K for 6 h under vacuum and then separately carbonized at 1073, 1123 and 1173 K for 4 h. The silica template was removed from the carbonized sample by treating with dilute HF or NaOH. The resulting carbon materials were denoted as OMCN_x . Here x represents the carbonization temperature in Kelvin.

Nitrogen adsorption–desorption isotherms were obtained at 77 K using an ASAP 2010 (Micromeritics) instrument. Pore-size distributions were determined by the BJH (Barret–Joyner–Hallender) method applied to the adsorption branches of isotherms. Pore structures and morphologies of OMCNs were examined by HR-TEM (JEM-3010, JEOL). To analyze the nitrogen states on the carbon surface, X-ray photoelectron spectroscopy (XPS) measurements were conducted with a SIGMA PROBE equipment (ThermoVG). The binding energies were calibrated with respect to C 1s (284.6 eV).

Electrochemical studies of OMCNs were performed using a conventional three-electrode system equipped with a saturated calomel reference electrode (SCE) and a platinum counter electrode. The working electrode ($1 \text{ cm} \times 1 \text{ cm}$) was prepared using 10 wt.% binding material (PTFE), 15 wt.% Ketjen black, and 75 wt.% OMCN_x . Cyclic voltammetry measurements were performed within the potential range of 0–0.7 V at a scan rate of 1 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ solution.

3. Results and discussion

Nitrogen adsorption–desorption isotherms of OMCNs are given in Fig. 1(a). The appearance of type-IV isotherms and nitrogen uptakes at relative pressures of 0.2–0.5 indicate that the prepared OMCNs have mesopores. It is noteworthy that the isotherms of OMCNs have two inflections in the adsorption branches at rela-

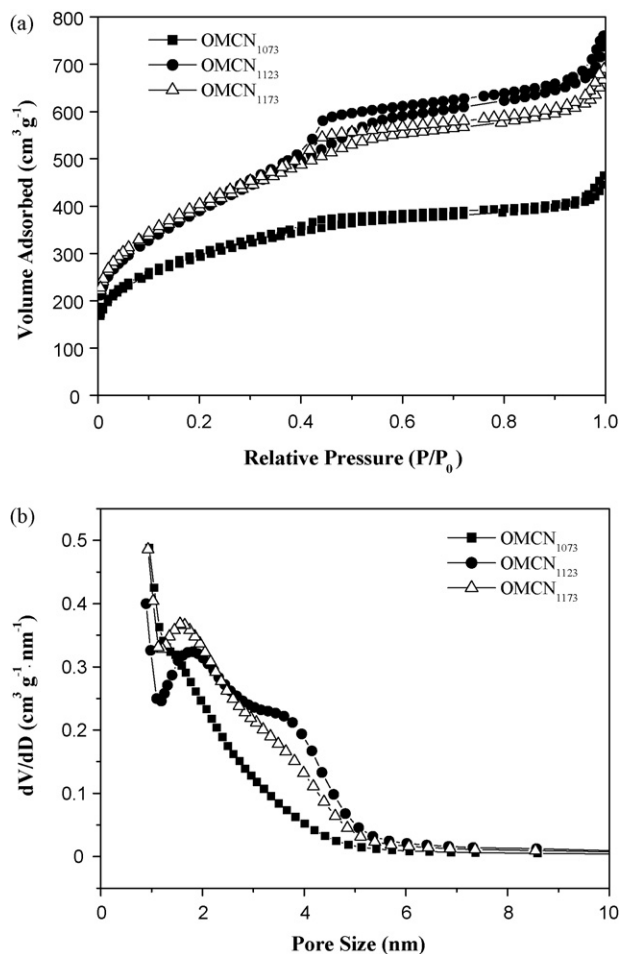


Fig. 1. (a) Nitrogen adsorption–desorption isotherms and (b) pore-size distributions of OMCNs.

tive pressures of 0.2–0.4 and 0.4–0.5 and this demonstrates that OMCNs have tube-type structures. Compared with rod-type carbon, tube-type carbon material has an additional inflection in the adsorption branch due to the existence of a bimodal pore structure. This is confirmed by the pore-size distributions. As shown in Fig. 1(b), bimodal pore structures centred at around 2 nm and 4 nm are observed.

The nitrogen adsorption–desorption isotherm and pore-size distribution of OMCN_{1073} show the destruction of the bimodal pore structure. The amount of adsorbed nitrogen is relatively small and the pore-size distribution centred at 4 nm is broad, compared with those of OMCN_{1123} and OMCN_{1173} . This result indicates that a low carbonization temperature of OMCN_{1073} provides insufficient energy to form a carbon framework and softens the carbon structure, resulting in the collapse of pore system [24,25]. On the other hand, OMCN_{1123} and OMCN_{1173} have a well-developed bimodal pore structure. The pores centred at 2 and 4 nm originate from the

Table 1

Physical properties and nitrogen states of OMCNs.

	Surface area ^a ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ^b ($\text{cm}^3 \text{ g}^{-1}$)	Pyridinic ^c (%) (398 eV)	Pyrrylic ^c (%) (400 eV)	Quaternary ^c (%) (401 eV)	Oxidized ^c (%) (402 eV)
OMCN_{1073}	1045	0.76	22.7	38.1	32.4	6.8
OMCN_{1123}	1420	1.21	20.2	26.0	37.5	16.3
OMCN_{1173}	1428	1.11	16.7	30.2	31.2	21.8

^a BET surface area.

^b Single point total pore volume.

^c Amount of each nitrogen species is calculated from the area of deconvoluted peak of XPS spectrum.

removal of the silica template and from the tube-type structure, respectively [23]. It should be noted that the pores of OMCN₁₁₇₃ caused by silica removal are smaller while those of OMCN₁₁₇₃ caused by the tubular structure are larger than those of OMCN₁₁₂₃. This implies that a high carbonization temperature induces shrinkage of silica and the carbon framework [26,27], resulting in an expansion of the inner pores and shrinkage of the outer pores of the tubular structure.

The physical properties of OMCNs are listed in Table 1. The surface area and pore volume of OMCN₁₀₇₃ are 1045 m² g⁻¹ and 0.76 cm³ g⁻¹, respectively, which are the smallest among the OMCN samples due to collapse of the pore structure. OMCN₁₁₂₃ and OMCN₁₁₇₃ have similar surface areas of about 1420 m² g⁻¹, but retain different pore volumes. The pore volume of OMCN₁₁₂₃ (1.21 cm³ g⁻¹) is larger than that of OMCN₁₁₇₃ (1.11 cm³ g⁻¹), due to shrinkage of the carbon framework of OMCN₁₁₇₃. The above result indicates that the carbonization temperature is an important factor in forming a well-developed pore structure and in determining the physical properties of OMCN. It can be concluded that the optimum carbonization temperature is 1123 K.

HR-TEM images of OMCNs are given in Fig. 2. Destruction of the pore structure is observed in OMCN₁₀₇₃. By contrast, OMCN₁₁₂₃ and OMCN₁₁₇₃ have a well-developed ordered mesoporous structure with a hexagonal array. The observed pore size of OMCN₁₁₂₃ and OMCN₁₁₇₃ is ca. 4 nm, in good agreement with nitrogen adsorption–desorption results.

N/C wt.% of OMCNs was determined by elementary analyses. Quinoline (carbon precursor) contains 9.7 wt.% nitrogen. Even after polymerization and carbonization, a relatively large amount of nitrogen remains. Some portion of nitrogen is removed as a volatile form of NH₃ during the polymerization of quinoline and the carbonization process [24,25]. The residual N/C wt.% of OMCN₁₀₇₃, OMCN₁₁₂₃ and OMCN₁₁₇₃ is 6.7, 5.9 and 5.4 wt.%, respectively. Hence, the nitrogen content of OMCNs decreases with increasing carbonization temperature.

The N 1s XPS spectra and deconvoluted peaks of OMCNs are shown in Fig. 3. Pyridinic, pyrrolic, quaternary and oxidized nitrogens appear at 398 ± 0.2, 400 ± 0.2, 401 ± 0.2, and 402 ± 0.2 eV, respectively. The amount of each nitrogen species is listed in Table 1. Most of the nitrogen in quinoline (carbon precursor) is in the form of pyridinic nitrogen. It is observed, however, that pyridinic nitrogen is chemically transformed into nitrogen species with higher binding energies (pyrrolic and quaternary states) during polymerization and carbonization. The nitrogen states on the surface of OMCNs are closely related to the carbonization temperature. With increasing carbonization temperature, the content of pyridinic states decreases and the content of oxidized states increases. It should be noted that OMCN₁₀₇₃ and OMCN₁₁₂₃ have the largest amount of pyrrolic nitrogen and quaternary nitrogen, respectively. The fraction of pyrrolic and quaternary states is important for application in EDLCs, due to their contributions to pseudocapacitance, wettability and hydrophilicity.

Cyclic voltammograms of OMCNs are presented in Fig. 4. The voltammetric curves of OMCN₁₁₂₃ and OMCN₁₁₇₃ have a rectangular-shape, which indicates ideal capacitance behaviour. By contrast, OMCN₁₀₇₃ gives a distorted voltammetric curve due to the destruction of the pore structure. It is known that nitrogen functional groups enhance the wettability of carbon by electrolyte via increases in the hydrophilic polar sites and the electrical conductivity [9,20,28,29]. OMCN₁₁₂₃ gives the most desirable double-layer capacitance behaviour, as evidenced by a more rectangular-shaped pattern and steeper current change at the switching potentials. This is attributed to the high content of polar species, i.e., quaternary nitrogen, as revealed by XPS analyses. On the other hand, OMCN₁₀₇₃, which has the smallest surface area, has a higher capacitance than OMCN₁₁₂₃ due to the pseudocapacitance effects of

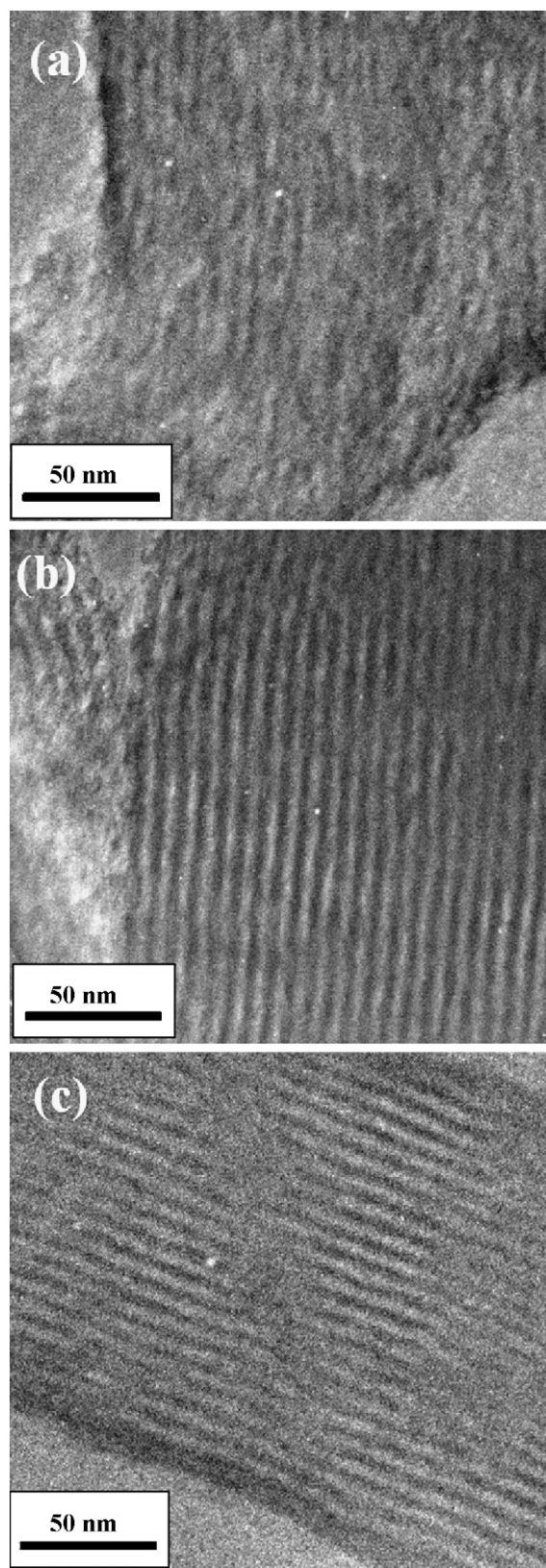


Fig. 2. HR-TEM images of (a) OMCN₁₀₇₃, (b) OMCN₁₁₂₃, and (c) OMCN₁₁₇₃.

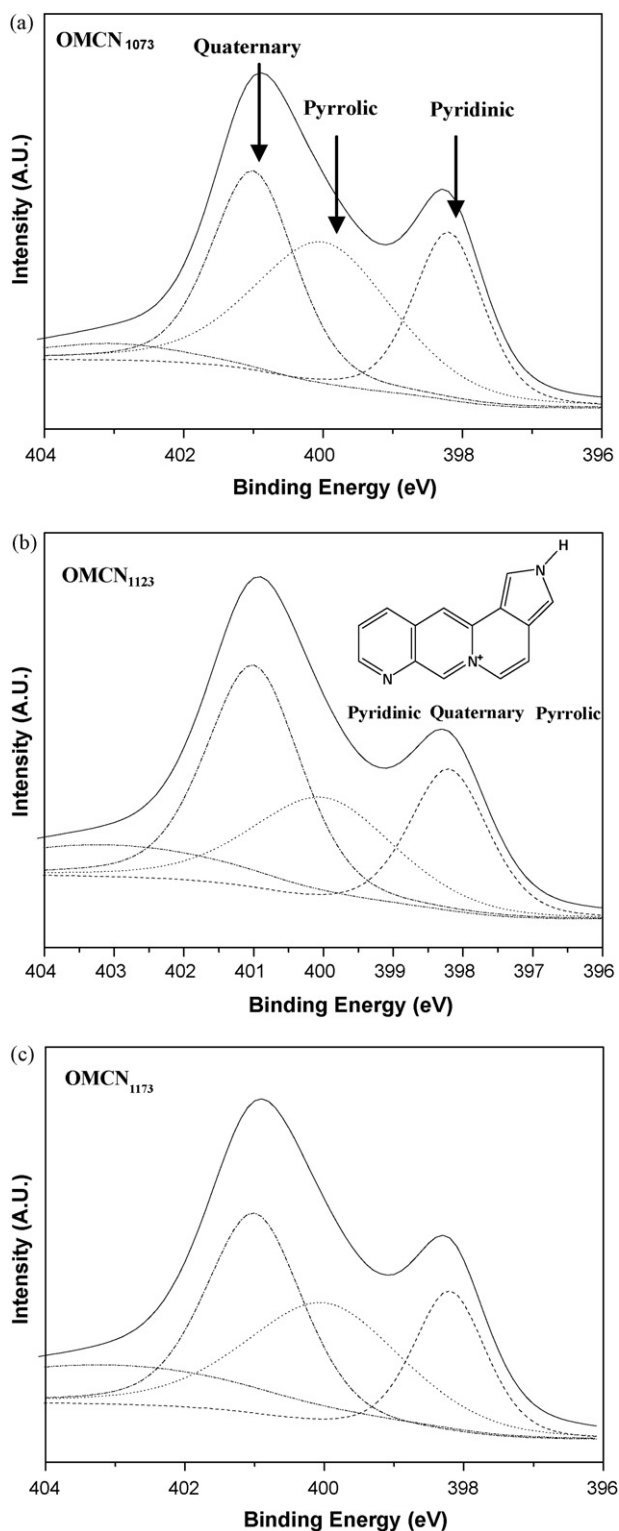


Fig. 3. N 1s core level peaks and deconvoluted peaks of (a) OMCN₁₀₇₃, (b) OMCN₁₁₂₃, and (c) OMCN₁₁₇₃.

pyrrolic nitrogen species. OMCN₁₁₇₃ exhibits the highest capacitance value, in spite of the smallest N/C wt.%. It is thought that the large contents of pyrrolic and oxidized nitrogen species in OMCN₁₁₇₃ play a positive role in the increase of pseudocapacitance. The capacitances of OMCN₁₀₇₃, OMCN₁₁₂₃ and OMCN₁₁₇₃ calculated from CV measurements are 105, 98 and 108 Fg⁻¹, respectively.

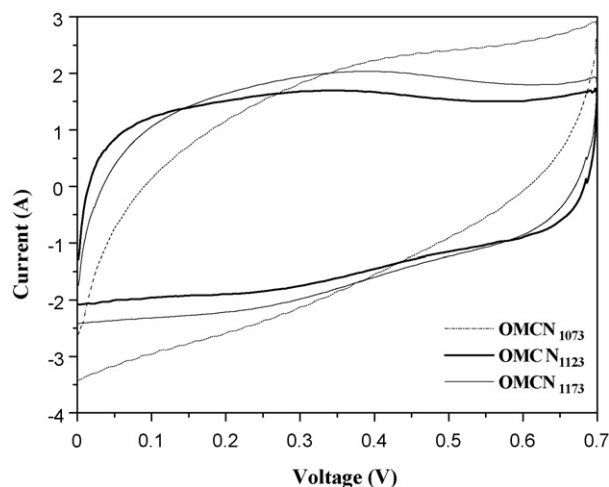


Fig. 4. Cyclic voltammograms of OMCNs in 1 M H₂SO₄ solution at scan rate of 1 mV s⁻¹.

4. Conclusions

Ordered mesoporous carbon nanopipes (OMCNs) with nitrogen functionality have been prepared using quinoline as a carbon precursor and Al-SBA-15 as a template. The carbonization temperature plays an important role in forming a carbon structure and in determining the physicochemical properties of OMCNs. The OMCN carbonized at 1123 K has high surface area, large pore volume, uniform pores, and a well-developed mesoporous structure. Increase in the carbonization temperature enhances the amount of nitrogen species with high binding energy. The nitrogen states affect the electrochemical properties of carbon materials and serve as an important factor for preparing an ideal EDLC. The OMCN samples prepared in this work are potentially available as useful candidates for fabricating EDLCs.

Acknowledgements

The work was supported by the Samwha Capacitor Cooperation, the World Class University program through the Korea Science and Engineering Foundation funded by the Ministry of Education, Science and Technology (400-2008-0230).

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