



Short communication

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

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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-

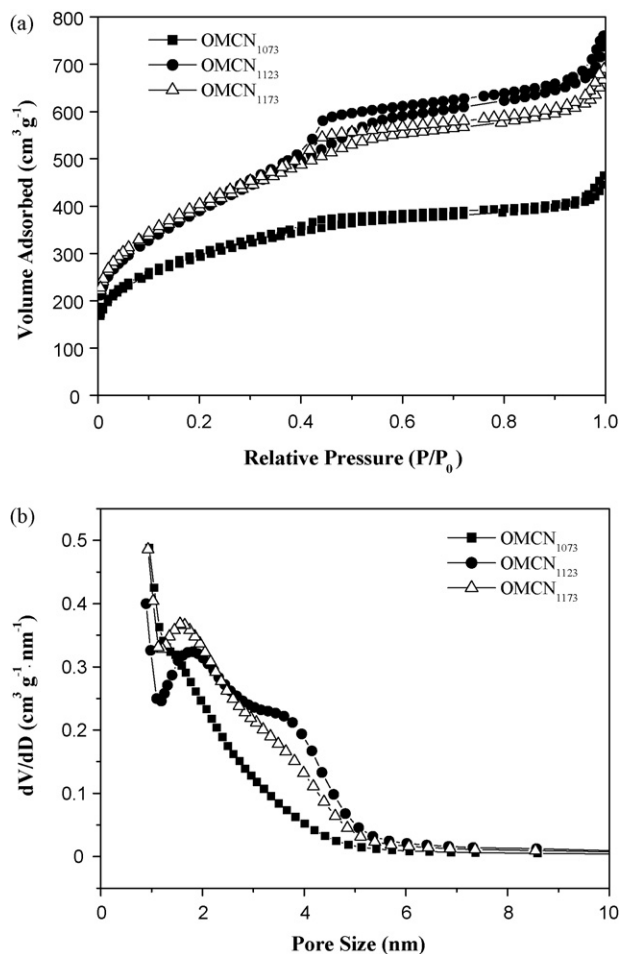


Fig. 1. (a) Nitrogen adsorption–desorption isotherms and (b) pore-size distributions of OMCNs.

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.

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