

Highly microporous carbon materials synthesized from fluorine-containing poly(amic acid) adsorbed in polystyrene cryogel template

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ABSTRACT

In this work, a highly microporous carbon material was synthesized through the combination of fluorine-containing poly(amic acid) (F-PAA), which can produce a microporous carbon material upon carbonization, and a mesoporous polystyrene (PS) cryogel. Carbonization of F-PAA at 1000 °C yielded a microporous carbon material with high specific surface area (SSA, ~1300 m²/g). In addition, we prepared a PS cryogel template with microcellular structure by freeze-drying the PS solution in 1,4-dioxane. The template was then impregnated with F-PAA, followed by carbonization at 1000 °C. Interestingly, the carbon material obtained through this approach maintained the microcellular structure of the PS cryogel template even after template pyrolysis during carbonization. Moreover, the microcellular carbon material exhibited a high SSA and a large micropore volume (~2400 m²/g and 0.90 cm³/g, respectively).

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1. Introduction

A unique method for producing highly ordered mesoporous carbon materials, based on microcellular carbon cryogels with honeycomb structure fabricated via uniaxial freeze-drying, has been proposed recently [1,2]. Since the solvents suitable for this approach are limited to water or 1,4-dioxane, only polymers soluble in these solvents, such as polyvinyl alcohol [3], polystyrene (PS) [4,5], polyurethane [6] and polylactide [7] were used to prepare polymer cryogels by freeze-drying. However, these polymers are not useful as carbonization precursors due to their low carbonization yield, and their microcellular morphology is not maintained after heat treatment. For this reason, only a few studies have involved the use of polymer cryogels to produce highly ordered carbon materials by freeze-drying [1,2,8]. Alternative approaches to prepare porous carbon materials by adsorbing additional carbon sources into a freeze-dried porous polymer cryogel template have been investigated [9,10]. However, the

porous carbon materials obtained from the polymer cryogel template were mesoporous and possessed a specific surface area (SSA) of ca. 800 m²/g, which is too low for the application of these materials as charge storage materials for electric double-layer capacitors (EDLC) [11].

Polyimides (PIs), synthesized by the thermal imidization of poly(amic acid) (PAA) precursors, have been considered as carbonization precursors because of their ability to retain the structural morphology even after carbonization, due to their homogeneous shrinkage, high carbonization yields, and absence of crack formation during carbonization [8,12]. This is a unique case where the molecular structure of the polymer precursors and the structural morphology of the polymer films control the structural morphology of the resulting carbon films. For these reasons, PIs have been used as carbonization precursors for the synthesis of highly oriented graphite films [13], macroporous carbon materials [14], and thin carbon membranes [15].

Recently, Inagaki *et al.* reported that PIs containing fluorine moieties exhibited a significantly enhanced microporous surface area when the fluorine content was increased [16]. The microporous surface area of PIs containing –CF₃ groups showed a strong dependence on the number of these groups in each PI repeating

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unit; moreover, the fluorine-containing PIs maintained the structure of the precursor after carbonization and possessed a high microporous surface area of 1400 m²/g.

The combination of fluorine-containing PAA (F-PAA) with the polymer cryogel template appears potentially interesting, because it could enable the production of carbon materials with high SSA by incorporating the high microporous surface area and microporous structure of the F-PAA within the microcellular and mesoporous structure of the polymer cryogel template. In this work, we prepared microcellular carbon materials by adsorption of the F-PAA solution into a microcellular PS cryogel template synthesized by the uniaxial freeze-drying. PS was selected as base material for the polymeric cryogel template because, whereas its low melting point and carbonization yield limit its use as a precursor for carbonization, it represents a suitable source material for the microcellular cryogel template.

2. Experimental

2.1. Materials

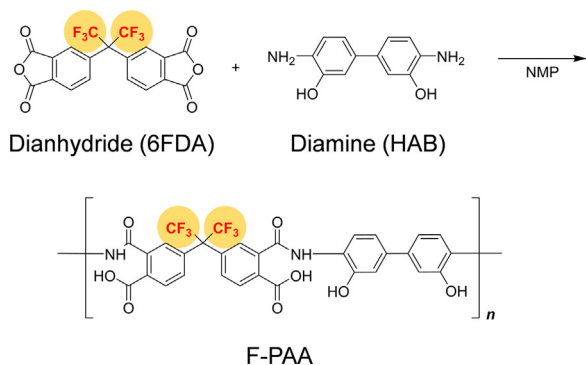
All experiments were performed in argon atmosphere. Polystyrene ($M_w = 280000$) was purchased from Sigma–Aldrich Co. (USA). *N*-Methyl-2-pyrrolidone (NMP) was distilled prior to use. Other chemical compounds such as 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 3,3'-dihydroxybenzidine (HAB) were purchased from commercially available sources.

2.2. Synthesis of F-PAA

The molecular structure of a repeating unit of F-PAA synthesized from 6FDA and HAB is shown in Scheme 1. First, HAB (0.49 g, 2.5 mmol) was dissolved in NMP (6 mL) and stirred at room temperature. 6FDA (1.0 g, 2.5 mmol) was then added dropwise to the solution at the same temperature. The mixture was stirred at the same temperature for 24 h and quenched with H₂O. The resulting precipitate was collected by filtration and dried in a vacuum oven at 60 °C for 24 h. The as-synthesized F-PAA showed good solubility in ethanol.

2.3. Preparation of the PS cryogel template

The PS cryogel template was synthesized by uniaxial freeze-drying, as shown in Scheme 2. The PS solution was prepared by dissolving PS (5 wt%) into 1,4-dioxane and transferred to a polypropylene (PP) test tube of 1.2 mm thickness, 100 mm length, and 10 mm diameter. The PS solution was then uniaxially frozen by dipping the test tube into a liquid nitrogen bath at a constant rate of 10 cm/h. After the dipping was complete, the frozen PS solution was freeze-dried at –5 °C for 3 days.



Scheme 1. Schematic molecular structure of F-PAA.

2.4. Preparation of microcellular carbon cryogel

The PS template/PAA complex was prepared by adsorption of a F-PAA ethanol solution (15 wt%) into the freeze-dried PS cryogel template at room temperature for 5 min. After the adsorption, the PS template/PAA complex was dried in a vacuum oven for 2 h at room temperature. These two processes were repeated 3 times. Then, in order to remove the PS cryogel template, the PS template/PAA complex was carbonized at 1000 °C under argon gas flow at a heating rate of 10 °C/min. The carbonized PS template/PAA complex will hereafter be abbreviated as TC-PAA. A reference RC-PAA sample was also prepared with a carbonized material from F-PAA, *i.e.*, without using the PS template.

2.5. Characterization

The structural morphology of the obtained samples was determined by a field-emission scanning electron microscope (FE-SEM, Nova Nano SEM 450, FEI Co., USA). Before the SEM analysis, the samples were frozen with liquid nitrogen to prevent transformation, and sectioned with a straight razor blade in both vertical and horizontal directions. Thermogravimetric differential thermal analysis (TG-DTA, TA instrument, USA) of PS cryogel template, freeze-dried F-PAA, and PS template/PAA samples was carried out under nitrogen gas flow at a heating rate of 10 °C/min. The specific surface area of carbonized F-PAA and PS template/PAA samples was measured by nitrogen gas adsorption (BELSORP-max, BEL Japan, Inc., Japan). The samples were also analyzed by Fourier-transform infrared spectroscopy (FT-IR, Nicolet iS 10, Thermo Scientific, USA). The electrical conductivity of TC-PAA was measured by a 4-point probe method (FPP-RS8, DasolEng, Korea).

3. Results and discussion

TG-DTA profiles of PS cryogel template, F-PAA, and PS template/PAA were measured from 0 to 950 °C under nitrogen gas flow at a heating rate of 10 °C/min (Fig. 1). According to the TG-DTA results, the degradation temperature and weight loss of the PS cryogel template were 400 °C and 99%, respectively. In the case of F-PAA, the weight loss occurred in two stages: the first stage in the 150–250 °C temperature range was associated to the imidization of the F-PAA precursor, whereas the second stage between 400 and 500 °C was attributed to the thermal conversion of PI to polybenzoxazole, owing to cyclodecarboxylation (–CO₂). Weight loss peaks of PS and PAA were observed in the TG-DTA curve of the PS template/PAA complex, and three sequential degradation peaks were observed in the temperature range of 350–700 °C. These peaks were mainly due to the breakage of carbonyl groups in the imide moiety. Based on the char yield determined from the TGA results, the mass fraction of the PS template/PAA complex was estimated in *ca.* 80 wt% of the total mass (at 300 °C), while the mass fraction of F-PAA in the PS template/PAA complex was estimated to be 52 wt% (at 480 °C). After thermal decomposition above 900 °C, a final weight of less than 32 wt% of the initial weight was determined from the TGA curve of the PS template/PAA complex.

Fig. 2 show the FT-IR spectra measured for the PS cryogel template, F-PAA, and PS template/PAA complex. The FT-IR spectra of the PS cryogel template exhibited characteristic peaks at 3040 cm^{–1} (ν_{C-H} , aromatic), 2918 cm^{–1} (ν_{C-H} , aliphatic), 1620 cm^{–1} ($\nu_{C=C}$, aromatic), 1457 cm^{–1} ($\nu_{C=C}$, aromatic), and 1070 cm^{–1} (ν_{C-H} , aromatic). In the case of F-PAA, peaks at 1645 cm^{–1} ($\nu_{O=C-NH}$, amide), 1520 cm^{–1} (ν_{N-H} , amide), 1410 cm^{–1} (ν_{C-N} , amide), and 1255 cm^{–1} (ν_{C-O} , phenol) were observed. The FT-IR spectra of the PS template/PAA complex exhibited peaks characteristic of both the PS cryogel template and F-PAA. For example, absorption peaks corresponding to the methylene

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