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Ordered mesoporous carbon membrane prepared from liquefied larch by a soft method

Xin Zhao, Wei Li, Shouxin Liu*

Key Laboratory of Bio-Based Material Science and Technology, Ministry of Education, Northeast Forestry University, Harbin 150040, China

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ABSTRACT

Carbon membranes having ordered mesoporous structure were prepared via liquefaction, resinification, assembly and carbonization steps using natural renewable larch sawdust as starting material. The mesopores of the carbon membranes were formed by assembly of larch-based resin with F127 (PEO–PPO–PEO). The mesoporosity was controllable from disordered to ordered by varying the carbonization temperature. Mesoporous carbon membrane with an ordered two-dimensional hexagonal porous structure having *P6mm* symmetry was obtained at 700 °C. The unique ordered mesoporous structure resulted in the carbon membranes exhibiting high efficiency (permselectivity factor =1.97) for the separation of CO_2 from a N_2/CO_2 mixture.

1. Introduction

The growing demand for green energy and efficient gas separation has attracted extensive research into the development of new membrane synthesis technologies and renewable starting materials. Gas separation using membranes relies on the thermal, chemical, and mechanical properties of the membrane materials. Recently, mesoporous carbon membranes (CMs) with ordered pores have appeared as promising candidates for gas separation due to their uniform pore structure [1].

Until now, ordered carbon membranes have usually been synthesized from synthetic phenolic resins using a soft-template strategy [2,3]. The hydroxyl groups of such phenolic resins interact with the PEO groups (polyethylene oxide) of the soft template F127 or P123 (PEO_n–PPO_m–PEO_n), and form ordered mesopores [4,5]. Considering the large availability and renewable characteristics of biomass such as waste wood, the liquefaction of wood as a replacement for phenol in the synthesis of novel carbon materials with specific morphology and porous structure has proved promising [6]. It is highly expected that wood components depolymerized through liquefaction processes and reacted with specific organic reagents will produce various value-added polymer precursors or chemicals [7]. However, the preparation of ordered carbons with tunable pore structure from wood remains a challenge due to the complex intrinsic natural characteristics of wood.

In the present work, we focus on the preparation of ordered mesoporous carbon membrane by organic-organic assembly of copolymer F127 with liquefied larch-based resins using an evaporation-induced self-assembly (EISA) strategy. The performance of the obtained carbon in the separation of CO_2 from a N_2/CO_2 mixture was investigated.

2. Experimental

Liquefaction of larch sawdust: The procedure used to prepare the liquefied larch sawdust was based on that reported in the literature [8]; 10 g of larch sawdust, phenol (30 mL), sulfuric acid (98%, 1 mL), and phosphoric acid (85%, 2 mL) were added to a three-necked glass reactor that was equipped with a mechanical stirrer, thermometer, and condenser. The mixture was heated under reflux at a temperature of 110–120 °C for 1 h. When the reaction was finished, methanol (120 mL) was added to the liquefied product. The mixture was then filtered, the pH was adjusted to neutral using sodium hydroxide, and the mixture was filtered again to remove the resulting precipitate. The filtrate was concentrated by vacuum distillation at 40 °C to remove the methanol, yielding liquefied larch wood.

Preparation of carbon membranes: In a typical synthesis, formaldehyde (37%, 90 mL) and sodium hydroxide (3 g) were added to the liquefied larch to generate larch-based resin under basic conditions. F127 (10 g) was then added and stirred for 20 h at 40 °C. Next, the pH was adjusted to 0.5 with HCl and the reaction was continued for 8 h at 50 °C. The obtained mixture was paved in ceramic ring matrices of 3 cm diameter and dried at 80 °C for 6 h.

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* Corresponding author. Tel./fax: +86 451 82191204.
E-mail address: liushouxin@126.com (S. Liu).

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Finally, the carbon membranes were formed after carbonization under a N_2 atmosphere at different temperatures (500 °C, 600 °C, 700 °C) for 2 h. The carbon membranes were denoted as CM-*x*, where *x* is the carbonization temperature.

Characterization: The morphology of the CMs was examined by scanning electron microscopy (SEM; QUATA 200, Zeiss, Japan) operating at an accelerating voltage of 15 kV. Transmission electron microscopy images were obtained on a JEOL 2011 (FEI, Holland) operated at 200 kV. Nitrogen sorption isotherms were measured with a Micromeritics ASAP 2020 sorptometer using nitrogen as the adsorbate at 77 K. Before analysis, all samples were degassed at 300 K for more than 10 h. The surface areas were calculated using the BET (multi-point Brunauer–Emmett–Teller) method using the adsorption data in the relative pressure (P/P_0) range of 0.04–0.2. The micropore surface area and volume were obtained using *t*-plot analysis. The pore size distributions (PSDs) were determined using non-local density functional theory (NLDFT), based on nitrogen adsorption data with a slit pore model.

Gas separation test: The permeation through the carbon membranes by CO_2 and N_2 gases was measured at ambient temperature (20 ± 1 °C). The carbon membrane (area $\approx 3 \times 10^{-4}$ m^2) was attached to a permeation cell and high-pressure ultra-pure gases supplied from compressed gas cylinders were placed in contact with the membranes. A manometer was used to measure the pressure. Vacuum was maintained on the low-pressure side of the membranes, and the permeation was pulled through a calibrated volume. The gas permeation and permeability of membranes was estimated from K (m^3 cm/m^2 h kPa) defined by

$$K = 45.8\frac{V\delta}{d^2\,\Delta P\,t} \tag{1}$$

$$a_{A/B} = \frac{K_A}{K_B} \tag{2}$$

where V is the permeate volume, here $27.79(H_2-H_1)$; ΔP is the pressure difference, where $\Delta P = (P_1+P_2)/2$; δ is the membrane thickness, d is the spherical diameter, and t is the experiment duration. $a_{A/B}$ is the gas permeability of the membrane for gases A and B.

3. Results and discussion

Transmission electron microscopy (TEM) images of carbon membranes carbonized at different temperatures are shown in Fig. 1a–c. Both disordered and ordered mesopores (centered at 2 nm), which were formed by assembly of the PEO groups in F127 with hydroxyl groups [4] from the liquefied larch and larch-based resin, were observed. According to the TEM images, the carbonization temperature has significant effects on the formation of the porous structure. CM-500 (Fig. 1a) shows a typical disordered mesoporous structure, while ordered mesopores with 1D channels are observed for CM-600 (Fig. 1b). At a further increase in carbonization temperature, CM-700 (Fig. 1c) exhibited well-ordered arrays in large domains, which indicated the formation of an ordered 2D hexagonal mesostructure with 1D channels. Because F127 decomposes at lower temperatures (< 400 °C), the formation of the porous structure is closely related to the degree of

Table 1
Structural parameters of CMs prepared at different carbonization temperatures.

Sample	S_{BET} (m^2/g)	S_{micro}/S_{BET} (%)	V_{total} (cm^3/g)	Average pore diameter (nm)
CM-500	367	80	0.198	2.15
CM-600	400	83	0.214	2.14
CM-700	469	87	0.250	2.13
CM-800	346	78	0.126	2.63

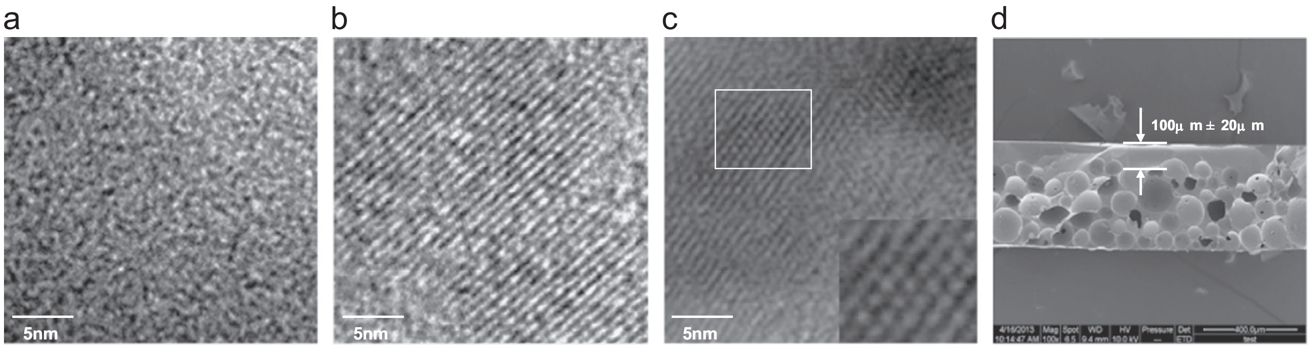

Fig. 1. TEM and SEM images of CMs prepared at different carbonization temperatures (TEM, a: CM-500; b: CM-600; c: CM-700; SEM, d: CM-700).

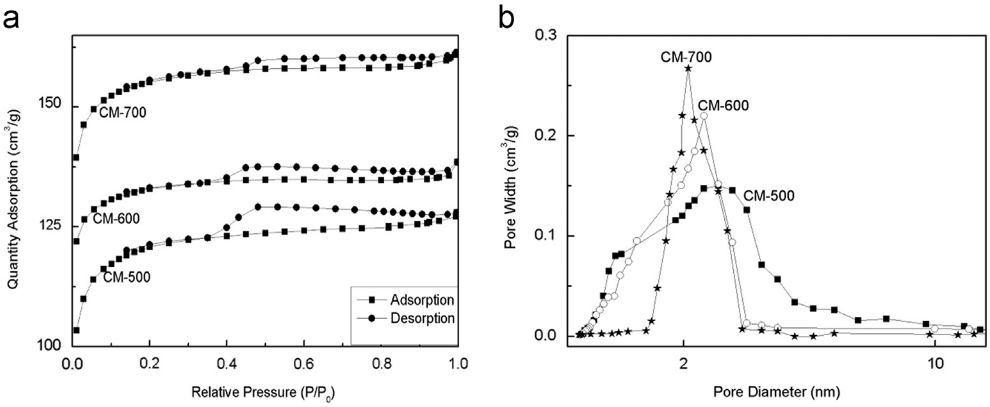

Fig. 2. Nitrogen adsorption–desorption isotherms and pore diameter distribution of CMs prepared at different carbonization temperatures.