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## Preparation and gas separation performance of supported carbon membranes with ordered mesoporous carbon interlayer

Lin Li<sup>a</sup>, Chengwen Song<sup>a,b,\*</sup>, Huawei Jiang<sup>a</sup>, Jieshan Qiu<sup>a</sup>, Tonghua Wang<sup>a,\*\*</sup><sup>a</sup> State key Laboratory of Fine chemicals, Carbon Research Laboratory, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China<sup>b</sup> School of Environment Science and Engineering, Dalian Maritime University, 1 Linghai Road, Dalian 116026, China

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## ABSTRACT

An ordered mesoporous precursor synthesized by the soft-templating approach has successfully been used to prepare a carbon interlayer between the thin separation layer and the support of carbon membranes. Morphology and pore structure characteristics of the ordered mesoporous carbon (OMC) interlayer were investigated by HRTEM, XRD, SEM and N<sub>2</sub> adsorption techniques. Gas separation properties of resultant supported carbon membranes were evaluated by single gas permeation experiments. The results showed that the OMC interlayer can effectively reduce surface defects of the support with large pore sizes, improve the interfacial adhesion of the support to the thin separation layer, and further enhance the gas permeation properties of the supported carbon membranes by ordered and uniform mesoporous channels. The supported carbon membranes were synthesized by one-step coating on the support modified by the OMC interlayer and achieved O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> permeances of 74.5, 88.0 and 545.5 mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> × 10<sup>-10</sup>, respectively. These are about 4 times higher than those without the interlayer and are very competitive with respect to other carbon membranes reported in literature. The results clearly indicate that this novel approach using the OMC as an interlayer to fabricate supported carbon membranes with macro-meso-microporous gradient structure have attractive potential for gas separation.

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## 1. Introduction

Membrane-based gas separation has demonstrated outstanding advantages over conventional cryogenic distillation and pressure swing adsorption in terms of low energy consumption, low capital investments, simple and easy operation, and compact equipment [1]. Currently, the dominant membrane materials used in industrial gas separation applications are polymeric membranes. However, the encountered challenges of harsh environments during membrane operation and the limitation of the trade-off between permeance and selectivity of polymeric membranes have prompted the search for more robust materials with higher permeance and selectivity. Porous inorganic membranes, exhibiting both molecular sieving properties and better selectivity, thermal stability and chemical stability, such as zeolite membranes, silica membranes and carbon membranes, have gained

considerable attention over the past several years. Silica membranes can selectively separate hydrogen from other gases but selectivity between similar-sized molecules, such as oxygen and nitrogen is not sufficient. Zeolite membranes can separate isomers, but it is difficult to obtain a large, crack-free zeolite membranes. Carbon membranes, as one of the most promising porous inorganic membranes, have demonstrated their outstanding role in gas separation processes [2–4]. It is not only due to their significant advantages that can separate gas molecules under harsh conditions (i.e., elevated temperature and pressure) but also due to their molecular sieving capability derived from their ultramicropore structure with the dimensions close to the size of permeating gas molecules, which help them to achieve a desirable and practicable selectivity [5–7]. Carbon membranes are typically prepared from inert or vacuum pyrolysis of various polymeric materials such as poly(furfuryl alcohol), phenolic resins, polyacrylonitrile, coal tar pitch, and polyimide. Among these, polyimide, synthesized by different types of dianhydrides and diamines, has been utilized extensively as the precursor to prepare carbon membranes. In general, carbon membranes can be grouped into two categories. Unsupported carbon membranes (flat, capillary or hollow fiber) [8–10] and supported carbon membranes (flat or tube) [11–13]. In the case of the former, carbon hollow fiber membranes are

\* Corresponding author at: State key Laboratory of Fine chemicals, Carbon Research Laboratory, School of Chemical Engineering, Dalian University of Technology, 2 Linggong Road, Dalian 116024, China. Fax: +86 411 84724342.

\*\* Corresponding author. Fax: +86 411 84724342.

E-mail addresses: [chengwensong@dlnu.edu.cn](mailto:chengwensong@dlnu.edu.cn) (C. Song), [wangth@dlnu.edu.cn](mailto:wangth@dlnu.edu.cn) (T. Wang).

preferable due to their low cost, high packing density and high separation performance from the standpoint of large-scale application. However, the brittleness of carbon hollow fiber membranes makes them difficult to handle, and limits their applications in membrane separation [14–17]. The supported carbon membranes are therefore regarded as the favored choice for commercial application of carbon membranes owing to their thin separation layer and high mechanical strength.

In the preparation of supported carbon membranes with excellent separation performance, the pore structure and surface roughness of the support play important roles in the formation of a uniform and defect-free thin separation layer [18]. The pore diameter of support should be about an order of magnitude smaller than the thickness of separation layer [15] and the surface of the support should be polished to reduce surface flaws and improve interfacial adhesion before coating [18]. Besides the uniform pore size distribution in the support, it is also necessary to make the coating solution easier to cover the surface of the support completely and form a uniform thin separation layer with high gas separation performance. For those reasons, the small pore diameter (SPD) supports, having usually less than  $\sim 0.2 \mu\text{m}$  with smooth surfaces, are preferably used. A defect-free thin separation layer could be formed on the support by one subsequent casting step in the fabrication of supported carbon membranes [17,19]. The large pore diameter (LPD) support with usually greater than  $\sim 0.2 \mu\text{m}$  and a rougher surface does not generally produce high-quality supported carbon membranes because it is prone to initiate interfacial defects during the formation of separation layer. Thus, several coating–pyrolysis cycles are required to reduce the surface defects and form a defect-free separation layer [20,21] which greatly reduces the gas permeance of the obtained supported carbon membranes. As a result, the low gas permeance of supported carbon membranes obtained on LPD or SPD supports can hardly satisfy practical separation requirements [22]. Solving these problems is still a big challenge for the commercial application of supported carbon membranes.

An effective solution may be to build a bridge between the thin separation layer and LPD support to improve their interfacial adhesion and enhance the structural stability and separation performance of supported carbon membranes. Ordered mesoporous carbon (OMC), a porous carbon material synthesized by nanocasting (hard-template) or self-assembly (soft-template) methods and carbonized at high temperature, can be a good candidate for this bridge. This is because of its regular mesoporous structure, narrow pore size distribution, high surface area, large pore volume and surface functional groups, among other properties [23–27]. An attempt to establish a framework of supported carbon membranes with macro–meso–microporous gradient structure was proposed in this study, in which the OMC was used as an interlayer (i.e., bridge) to link the thin separation layer and support by improving the interfacial adhesion between them.

In this work, an ordered mesoporous precursor synthesized by the soft-template method was first coated on LPD coal-based carbon disk and carbonized to form the OMC interlayer. Then the poly(amic acid) (PAA), which exhibited an outstanding gas separation performance in preparation of carbon membranes due to its high thermal stability and high carbon residues, was coated on the top and carbonized to form a thin separation layer, and finally, the supported carbon membranes with unique macro–meso–microporous gradient structure were fabricated. The specific objective of the present study was to establish the interlayer as a bridge to link the thin separation layer and support and

discuss the influence of preparation parameters (e.g., R/F127, synthetic temperature, OMC precursor solution concentration) on structure and gas permeance of the OMC interlayer in detail. Also, gas permeance and selectivity of supported carbon membranes with the ordered mesoporous interlayer are compared to those without the interlayer. Results of this work indicate that introduction of the OMC interlayer between the separation layer and LPD support can greatly improve the gas permeance of the resultant supported carbon membranes by reducing the gas diffusion resistance through the membranes. With this novel approach, highly permeable and defect-free supported carbon membranes for gas separation can easily be derived.

## 2. Experimental

### 2.1. Materials

Coal powder was provided by Ningxia Coal Mine. Triblock copolymer Pluronic F127 (PEO<sub>106</sub>–PPO<sub>70</sub>–PEO<sub>106</sub>) (MW = 12,600) was purchased from Sigma–Aldrich Corp. Resorcinol (R) was supplied from Tianjin Damao Chemical Reagent Factory. Formaldehyde (37 wt%) (F) was bought from Shenyang Lianbang Chemical Reagent Factory. HCl (37 wt%) was obtained from Beijing Beihua Fine Chemical Co., Ltd. Ethanol was purchased from Tianjin Fuchen Chemical Reagent Factory. PAA was purchased from Tianjin Insulation Materials Factory. Dimethylacetamide (DMAc) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. All chemicals were used as received without any further purification.

### 2.2. Preparation of disk-shape support from cheap coal

The coal was used to prepare the support, in which fine particles were blended with a binder and pressed at 20 MPa in a static press to form a disk-shape support of 40 mm in diameter and 2 mm in thickness. After drying, the disks were carbonized to 900 °C at the rate of 3 °C/min and held for 30 min in an Ar atmosphere and cooled down to room temperature naturally. Properties of resultant carbon disks are listed in Table 1.

### 2.3. Preparation of supported carbon membranes

The polymeric precursor of the OMC was synthesized by an organic–organic self-assembly method using resorcinol (R) and formaldehyde (F) as the carbon precursor and F127 block polymers as the soft template, according to literature [28]. This mixture was used as the coating solution, which was diluted by dimethylacetamide (DMAc), to form an interlayer on the disk by the spin-coating method. After drying, it was carbonized to 800 °C at the rate of 1 °C/min in an Ar atmosphere and held for 2 h before cooling down to room temperature. Poly(amic acid) (PAA) precursors derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) in DMAc were stirred at room temperature for 12 h under a nitrogen atmosphere to obtain a homogeneous and viscous PAA solution [29]. Then, the PAA solution was coated on the disk with the interlayer by spin-coating method to form the thin top layer. The supported carbon membranes were heated at room temperature at a heating rate of 2 °C/min to 400 °C and held at this temperature for 60 min and then continued to be heated at a rate of 2 °C/min to the temperature of 700 °C in the

**Table 1**  
Properties of coal-based carbon disk supports.

Sample	Diameter (mm)	Thickness (mm)	Porosity (%)	The largest pore size ( $\mu\text{m}$ )	N <sub>2</sub> Permeance ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1} \times 10^{-10}$ )
Support	40	2	33.9	0.71	22,000

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