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Electro-casting aligned MWCNTs/polystyrene composite membranes for enhanced gas separation performance

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ABSTRACT

Embedding particulate fillers in the matrix of membranes have proven effective in improving their gas separation performance. To further improve the membrane performance, this study explores the possibility of aligning the fillers in membranes with the assistance of an alternating electric field. Composite membranes with different contents of multi-walled carbon nanotubes (MWCNTs) dispersed in polystyrene (PS) have been prepared via electro-casting, in which an alternating electric field of 2000 V/cm is vertically exerted on the thin layer of pre-membrane solution until the solvent is evaporated completely. The electro-casting results in not only vertical alignment, but also more uniform dispersion of MWCNTs in the membranes. The electro-cast composite membranes exhibit higher oxygen and nitrogen permeability, but the increment of the former is higher than that of the latter, resulting in improved selectivities of the membranes.

1. Introduction

Gas separation by membranes has been generally accepted as a more cost-effective, energy-efficient, intensification-easy and environmentally benign process compared to the traditional methods of gas separation [1,2]. However, there exist selectivity and permeability tradeoffs for most gas separation membranes, with the upper bound of tradeoff curves being first demonstrated by Robeson in 1991 [3] and renewed in 2008 [4]. To push up the upper bound, embedding particulate fillers in the matrix of membrane was attempted by many researchers [2,5–12].

The particulate fillers commonly incorporated in composite membranes are zeolites, carbon molecular sieves, activated carbons, silica, metal oxides, fullerenes and carbon nanotubes (CNTs) [8], among which CNTs are heavily favored because of their good mechanical properties, large specific surface area and smooth surface [13,14]. The excellent mechanical properties of CNTs arise from their carbon-carbon bond, which is among the strongest chemical bond known in nature. For this reason, the mechanical properties of CNTs composite membrane can be greatly improved even with a very low content of CNTs. Ruan et al. [15] showed that 1 wt% pristine MWCNTs dispersed in polyethylene film could increase the strain energy density by 150% and ductility by 140%, respectively. The surface areas of CNTs, especially MWCNTs, are quite large and their inner channels and interlayer spaces provide plenty of possible selective adsorption sites for gas molecules [16,17]. The smoothness of CNTs channels can contribute to highly efficient gas transport through the composite membranes. Kim et al. [18] reported that gas permeation was enhanced by at least 12% when 2 wt% open-ended CNTs were dispersed in poly(imide siloxane), while such effect was not observed in membranes embedded with close-ended CNTs. Besides, the results from molecular dynamic simulations indicated that the transport rate of gas in the smooth channels of CNTs was orders of magnitude larger than in other similar-sized nanoporous materials [19–22].

On the other hand, MWCNTs tend to aggregate in the polymer matrix, as in the case of polyether sulfone and modified MWCNTs composite membranes studied by Ge et al. [23]. These MWCNT aggregates can lead to the decrease of membrane permselectivity, as gas would transport through the large voids inside and between the aggregates. Moreover, the interfacial voids between the MWCNTs and the polymer would only provide discontinuous and tortuous paths for gas transport when the MWCNTs are randomly dispersed in the polymer matrix. Therefore, it is desirable to disperse the MWCNTs homogeneously in the membrane and align them vertically to the membrane surface, to take full advantage of MWCNT

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fillers and maximize membrane permselectivity. It is already known that CNTs in a polymer matrix can be aligned by using a magnetic field [24] or electric field [25], which exerts a twisting force on the CNTs and/or causes dipole–dipole interactions among them. Particularly, previous researches showed that it was possible to improve the gas permeability of MWCNT embedded membrane by aligning the MWCNTs in the membrane with a static electric field [14,26–28]. However, only a very limited number of membrane materials and gases have been tested and the effects of MWCNT content have not been reported so far, to our best knowledge.

In this paper, we report aligning the MWCNTs in membranes by means of an alternating, instead of static, electric field to avoid possibly uneven dispersion of the MWCNTs by electrophoresis. The permeation of oxygen and nitrogen through aligned MWCNTs/PS composite membranes of different filler contents have been investigated. The alignment of MWCNTs embedded in PS membranes is characterized using fluorescence spectrophotometry, combined with the measurement of the membranes' through-plane electric resistivity. The responses of MWCNTs to the electric field and the dispersion of MWCNTs in membranes have been observed via stereo microscopy method.

2. Experimental

2.1. Materials

Polystyrene (PS, Mw=280,000) was purchased from Sigma-Aldrich and used as received. Multi-walled carbon nanotubes (MWCNTs, 1–2 μm in length and 40–60 nm in diameter, purity ≥95%), were purchased from Shenzhen Nanotech Port Co., Ltd. Tetrachloroethylene (TCE, analytical grade), was supplied by Tianjin Guangfu Fine Chemicals Research Institute and used as received.

2.2. Membrane preparation

The received pristine MWCNTs were ultrasonically treated by an ultrasonic cell pulverizer (II-D Scientz Biotechnology Co., China) for 3 h to cut the MWCNTs into shorter pieces. MWCNTs and PS composite membranes were prepared via a solution electro-casting process: First, PS granules (0.4 g) were dissolved in TCE (7 g) under magnetic stirring for 12 h, resulting in a polymer solution, which was labeled as Solution A; Then, the treated MWCNTs were dispersed in 3 g of TCE under ultrasonication for 1 h to get a homogeneous mixture, which was labeled as Slurry B; Solution A and Slurry B were mixed and sonicated for 30 min to obtain a homogeneous casting solution; The solution was poured on a clean glass plate, which was then placed in between two parallel electrodes (as shown in Fig. 1); The solution was dried in a vacuum oven at 60 °C for 4 h and then 80 °C for 6 h, while exposing to a 2000 V/cm alternating electric field at 1 Hz

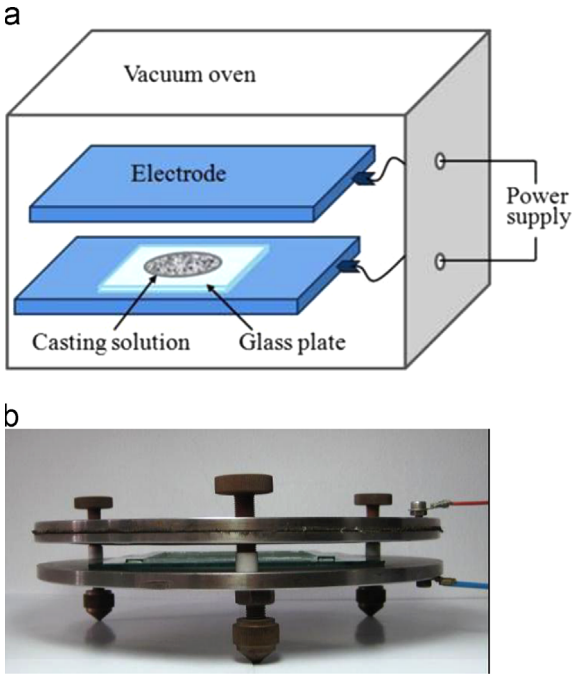

Fig. 1. Apparatus for electrical alignment of MWCNTs in polymer matrix. (a) A schematic and (b) a photo of the two electrodes and the glass plate.

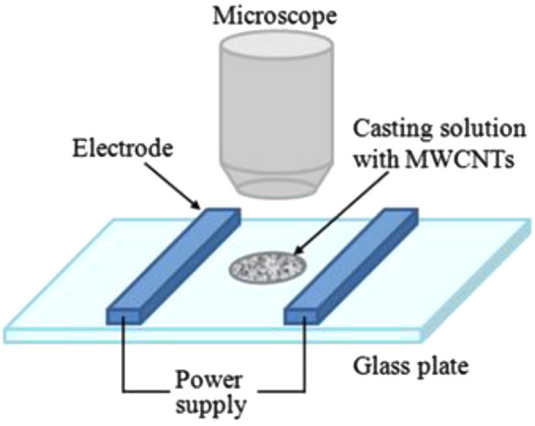

Fig. 2. Setup for observing the response of MWCNTs to electric field.

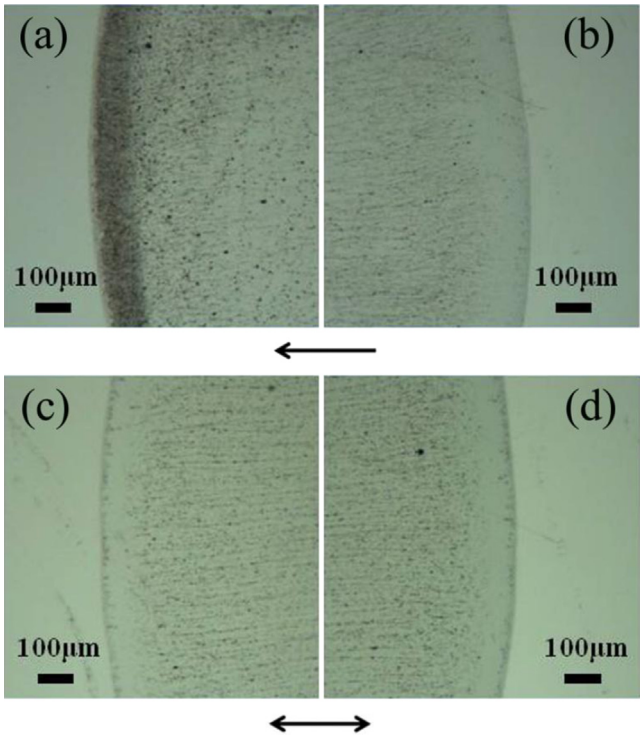

Fig. 3. Micrographs of local profiles of MWCNTs in a drop of 0.1 wt% MWCNTs casting solution near the two electrodes. The arrow indicates the direction of the electric field. (a) and (b): MWCNTs accumulate on the left side after migrating for 10 min along the direction of a 2000 V/cm static electric field; (c) (d): MWCNTs remain symmetrically distributed on both sides after exposing to a 2000 V/cm, 1 Hz alternating electric field for 10 min.