Journal of Membrane Science 460 (2014) 91–98

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Fabrication of flexible, aligned carbon nanotube/polymer composite membranes by in-situ polymerization

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ARTICLE INFO

Article history:
Received 19 September 2013
Received in revised form
8 February 2014
Accepted 12 February 2014
Available online 19 February 2014

Keywords:
Carbon nanotubes
Nanocomposites
Membrane
Separations
Nanofluidics

ABSTRACT

Vertically aligned (VA) carbon nanotubes (CNTs) have shown orders of magnitude enhancement for gas and liquid flow compared to conventional mass transport theories. Flexible, large surface-area VACNT membranes may provide a cost-efficient solution to various separation processes such as water purification and gas separation. However, all the VACNT membranes produced so far suffer from rather small membrane area, long fabrication process, poor mechanical stability, local agglomeration of CNTs, and low CNT packing density. Here, we present flexible, VACNT/polymer composite membranes having relatively densely packed CNTs as the only mass transport paths. In order to prevent CNT condensation that could disturb CNT orientation during liquid phase processing, we developed a novel in-situ bulk polymerization method to prepare VACNT/polymer composite films. A VACNT array was infiltrated with styrene monomer with a certain amount of polystyrene–polybutadiene (PS–PB) copolymer that acts as a plasticizer. Indeed, micro-indentation measurements confirmed that the addition PS-b–PB copolymer into the matrix improved the elongation at break of the CNT/PS composite film. SEM images showed that well aligned CNTs were embedded in a high-density polymer matrix free of any macroscopic voids or structural defects. Measured fluid rates and selectivity for gas and liquid mixtures are consistent with CNT membranes produced with different methods. These CNTs/polymer composite membranes showed high gas and water permeability comparable to the other VACNT composite membranes, potentially enabling applications that may require membranes with high flux, flexibility and durability.

1. Introduction

Exceptional electrical, thermal, mechanical, and mass transport properties of CNTs [1–7] make the CNTs a promising nanoporous material for applications in membrane separation. One-dimensional graphitic nanochannel structure of CNTs is of particular interest as a building block for the next generation membranes [5,6,8–12]. Exciting predictions from molecular dynamics simulations have motivated fabrication of CNT membrane platforms to develop new membrane materials with extremely large gas or water permeation. Hummer et al. have found that water molecules could transport in a single-file configuration through narrow CNTs at ultrahigh rates due to molecular ordering and tight hydrogen bonding under extreme graphitic nanoconfinement [13]. Atomistic simulation studies by Sholl et al. have also predicted unprecedentedly large gas permeation and selectivity of CNTs due to their atomically smooth wall and preferential gas–wall interactions [14].

Several research groups have experimentally verified predictions of MD simulations by employing CNT membranes fabricated by different methods. Hinds et al. first fabricated multi-walled VACNT (MWCNT) membranes with an inner core diameter of ca. 6 nm embedded in a rigid polystyrene matrix [5]. They demonstrated that liquid transport through the MWCNT membrane was several orders of magnitude faster than predictions from the classical hydrodynamics theory [15]. Holt et al. have adopted a micro-fabrication method [6] to produce membranes in which 1.6-nm-wide double-walled CNTs (DWNT) serve as only through-pores spanning a silicon nitride matrix deposited by chemical vapor deposition (CVD). Reported values of liquid and gas flows in DWNTs were several orders of magnitude larger than predicted

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http://dx.doi.org/10.1016/j.memsci.2014.02.016
0376-7388

by conventional hydrodynamics and Knudsen diffusion model, respectively. Yu et al. have used a matrix-free approach to fabricate CNT membranes [11]: capillary forces during solvent wetting and evaporation from as-grown CNT arrays produced small-size CNT mats with densities a few orders of magnitude higher than in other CNT membranes. Marand and coworkers developed a scalable, fabrication method, in which a preferential vertical alignment of single-walled CNTs (SWNTs) was achieved during filtration of a SWNT dispersion through a porous membrane, followed by sealing of the inter-SWNT spacing with polysulfone or polyacrylate copolymer [9,16,17]. The prepared SWNT membrane showed a CO_2/CH_4 mixture selectivity differing from the ideal gas selectivity, suggesting non-Knudsen transport through the SWNT interior. In another work, Wu and Hinds [18] have thoroughly mixed bulk nanotubes with epoxy resin and cut the cured CNT/epoxy composite into a 5-μm-thick slice using a microtome. More recently, Mauter et al. have used a magnetic field to orient liquid crystal mesophases of hexagonally packed cylindrical micelles and to template the alignment of SWNTs sequestered in the micellar cores [12].

Table 1 summarizes pros and cons of typical vertically aligned CNT (VACNT) membrane fabrication techniques. Unfortunately, all the CNT membranes produced so far suffer from at least one of the following drawbacks: (1) low density of CNT pores [16,19], (2) only partial CNT vertical alignment [16], (3) a brittle matrix [5,6], (4) rather small membrane active area and long fabrication processes [6], and (5) blocking of a large fraction of the pores by catalyst nanoparticles [19], excess matrix material [9], or polymerization inside the nanochannels [16]. These issues have hampered widespread successful production of CNT/polymer composite membranes that fully exploit the transport properties of the CNT channels. Hence, there still exists an impelling need for the development of defect-free, flexible, large active-area CNT membranes with well-aligned nanotubes and large pore density.

Choices of the polymeric matrix and specific processing steps are crucial for the successful fabrication of such CNT membranes. Liquid-phase processing such as the infiltration of a polymer solution into a CNT array often results in uneven CNT condensation, defects in polymer matrix, and loss of vertical CNT orientation during capillary condensation induced by solvent evaporation (Fig. S1). One promising approach for controlling CNT alignment during the polymer composite fabrication is to infiltrate monomers into the pre-aligned nanotube array, followed by in-situ polymerization [20,21]. By adopting this method here we overcome the typical limitation of polymer solution processes and demonstrate flexible, aligned-CNT/polymer composite membranes having relatively-high density CNTs. In our novel in-situ bulk polymerization method, end-protected vertically-aligned CNT arrays were infiltrated with styrene monomer with a certain amount of polystyrene–polybutadiene (PS-b–PB) block copolymer that acts as a plasticizer. A membrane matrix without larger structural defects obtained in this way combined high surface conformity with tunable flexibility. By adding PS-b–PB, the mechanical properties of the membrane were improved. Scanning electron microscopy (SEM) analysis also confirmed that alignment of CNTs remained undisturbed during the polymerization. These CNTs/polymer composite membranes showed very large gas and water permeabilities similar to those observed from the VACNT membranes reported in literatures [5,6,9,16,19,22], posing great promise in membrane applications that demand high flux, flexibility and durability.

2. Experimental

2.1. Membrane fabrication

The procedure for CNT/polymer composite membrane fabrication is shown in Fig. 1(a). To maintain nanotube alignment during styrene monomer infiltration into CNT mats, a wet PVA (89% hydrolyzed, Sigma-Aldrich) film of ca. 500 μm in thickness was gently attached on the top of CNTs. The assembly was dried under a vacuum to remove any water in the PVA film. The assembled PVA/CNT array was placed between two glass slides with PTFE spacers and the mold was sealed using a 20 wt% PVA solution as glue (Fig. 1(b)). The desired amount of PS-b–PB block copolymer (PS-block–PB-block–PS, styrene 30 wt%, Mw ~ 140,000, Sigma-Aldrich) was dissolved in styrene monomer (Sigma-Aldrich) with magnetic stirring. After 10 h of mixing, 0.5 wt% of 2,2′-azobisisobutyronitrile (Sigma-Aldrich) was added to the styrene monomer and PS-b–PB block copolymer mixture. The prepared mixture was injected into the mold and polymerized at 80 °C for 10 h in an argon-purged oven. Removal of the CNT/polymer composite from the mold could be easily achieved by dissolving PVA in warm water. The composite of polymer and CNT arrays was removed from silicon wafer with a 10 vol% HF solution. A reactive ion etching (RIE) plasma (Samco, RIE-1C), using 4:1 ratio of CF_4/O_2 at 10 W power, was used to clean sample surfaces as well as to open the CNT ends (Fig. 1(c)).

Table 1
Typical vertically aligned CNT membrane techniques reported in the literatures.

CNT	Pore diameter (nm)	Matrix/fabrication method	Density ($\times 10^{10}$ cm^{-2})	Advantages	Disadvantages
Post aligned SWNT [16]	1.2	Polyacrylate copolymer/ in-situ polymerization	0.7	• Scalability	• Low CNT density • Partial CNT alignment • Possible CNT damage during the cutting process
CVD-DWNT [6]	1.6	SiN_x/CVD	25	• Fast flux • Large flux enhancement	• Complicated membrane fabrication process • Poor mechanical properties
CVD-MWNT/alumina [19]	6.3	Polystyrene/solution casting	0.19	• Scalability/simple process	• Low CNT density • Low flux
CVD-MWNT [5]	7.0	Polystyrene/solution casting	6	• Fast flux • Large flux enhancement	• Poor mechanical properties
Carbon pipes [22]	43	CVD deposition of carbon on anodic aluminum oxide	1.07	• Simple process	• Poor mechanical properties • Low flux enhancement