



The most densified vertically-aligned carbon nanotube membranes and their normalized water permeability and high pressure durability



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ABSTRACT

Vertically aligned (VA) carbon nanotubes (CNTs) could be a promising material for membrane filtration due to their ultrahigh water permeability. However, VA CNT based membranes showed three challenging issues: low pore density, poor mechanical strength, and a complex fabrication process. In this study, the highest pore density 3.0×10^{12} pore/cm² was achieved by combining volatile ethanol addition and subsequent mold pressing. Urethane monomer was infiltrated between CNTs through an ethanol stream. Polymerized urethane provided mechanical strength to the VA CNT membrane. Membrane pore size distribution was analyzed based on the polyethylene oxide rejection. Pore size distribution ranged from 3.0 to 5.5 nm and the average pore size was 4.1 nm. The pressure durability representing mechanical strength was analyzed based on the compaction index (CI). The VA CNT membrane showed 4 times higher CI than that of the commercial ultrafiltration (UF) membrane due to its reinforcement. The VA CNT membrane showed 938 times higher water permeability than the UF membrane. Water permeabilities of all VA CNT membranes studied until now were compared using normalized forms based on the membrane pore structural parameters in the Hagen–Poiseuille (HP) equation. The results demonstrated that the VA CNT membrane fabricated in this study showed the highest water permeability enhancement and membrane pore size showed the highest deviation from HP theory among three structural parameters.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], synthesis processes have been developed stepwise for commercialization. The chemical vapor deposition (CVD) method developed in 1998 [2] can easily control the structure and morphology of CNTs at a lower temperature, including vertical orientation, and has been applied in various industries. As semiconductors, CNTs do not need a doping process and they can provide significantly higher integrity. Their higher thermal conductivity can release heat effectively, resulting from critical calculation. Their higher mechanical strength, surface area, and electrical conductivity show promising potential for the membrane in fuel cell stacks [3]. CNTs are also promising materials as membranes for water and wastewater treatment, with many potential advantages such as outstanding chemical-resistance, adsorption, and anti-biofouling properties. However, superfast water transport (i.e. more than several orders of magnitude of water transport enhancement relative to water transport calculated from continuum hydrodynamics [4]) through

inner pores of CNTs is the most attractive property.

Two directions [5], “ultrahigh-permeability” and “fouling-resistance”, were suggested for overcoming high energy consumption in membrane operation. Vertically aligned (VA) CNT membranes were introduced as promising candidates satisfying these requirements, along with forward osmosis and aquaporin membranes [6]. Ultrahigh water permeability of VA CNT membranes was demonstrated in two prior experiments [4,7] and explained by several computational simulations [4,7–10]. CNT has been composited with polymethylmethacrylate, polyvinylalcohol, polysulfone, and polyethersulfone based membranes [11–17]. These membranes showed the enhancement of antibiofouling property while maintaining high virus rejection and the possibility of application to sea water desalination.

Besides CNT-based composite membranes, VA CNT membranes using inner holes as membrane pores have rarely been studied, owing to their challenging fabrication processes. Since the introduction of the VA CNT membrane [7], two approaches have been attempted to fabricate high pore density membranes: the application of small pore size VA CNTs [4] and the densification of VA CNTs [18]. The former showed high pore density of 2.5×10^{11} pore/cm², but the fabrication process using silicon nitride (SiN_x) was too complex. The latter used the densified

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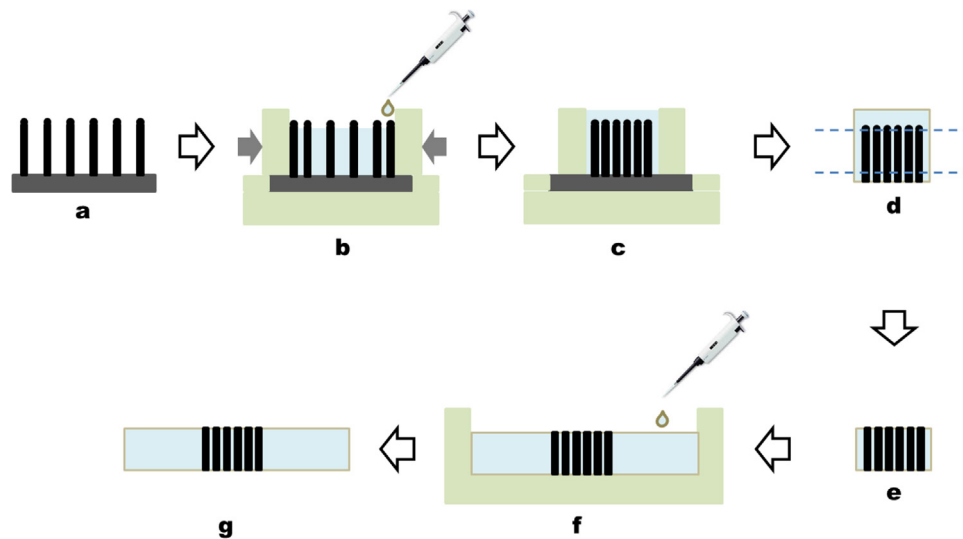


Fig. 1. VA CNT membrane fabrication procedure; VA CNT forest grown by CVD (a) were fabricated to densified VA CNT membrane (g). Urethane monomer was mixed with ethanol at 3:7 volume ratio and instilled into VA CNT on a mold (b). Ethanol acted not only as a densification agent, but also as a guide for the bulky urethane monomer in the interstitial space between CNTs. The densification was maximized by pressing the mold walls. Urethane monomer was cross-linked in the interstitial space of CNTs at 40 °C for 12 h (c). After the reaction, the top and bottom of the CNT membrane were cut using a microtome (d) and the membrane edge of the VA CNT membrane (e) was extended by additional cross-linking of UC-40 A, B (f).

interstitial space in which gaps were reduced from 30 to 3 nm to provide additional membrane pores without any sealing material. This resulted in 2.9×10^{12} pore/cm², which was 10 times higher than the former [7], but there was no support layer to maintain the mechanical strength against hydraulic pressure. Recently, a free-standing VA CNT membrane was fabricated by shear pressing from a roller [19], but it was operated under vacuum condition due to low pressure durability. For sufficient mechanical strength, VA CNT membranes should be filled with rigid materials as the reinforcer. The filling processes were divided into material phases. The first was the gas filling phase, with gases such as SiN_x [4]. Very small molecules in the gas phase efficiently filled the interstitial space between CNTs; however, the fabrication procedure was complex. The second was the liquid filling phase, with liquids such as diverse polymers [7,20,21]. They showed a very simple fabrication procedure but less filling efficiency resulting from the polymer's larger size and viscous flow. However, in all cited former studies on VA-CNT membranes, the demand for a simple and efficient reinforcer filling procedure had still not been met. Taken together, simple methods for fabricating VA CNT membranes with high density and high mechanical strength have not been introduced.

The primary objective of this study was to develop a simple method for fabricating VA CNT membranes with high pore density while maintaining high mechanical stability. To this end, we combined two approaches: densification of VA CNTs and a filling reinforcer. Ethanol was used for both CNT densification and monomer infiltration. The monomer could better enhance the filling efficiency of the space between CNTs than the polymer. After filling, the monomer was polymerized to show good mechanical stability. The addition of the mixture of monomer and ethanol could simplify the membrane fabrication process. The densification of VA CNT and reinforcement by a cross-linked polymer could show the synergistic enhancement of water permeability and mechanical stability of the VA CNT membrane.

Water transport through VA CNT membranes has been shown to follow a non-Hagen–Poiseuille (HP) relationship [4]. For example, a 4 mm thick VA CNT membrane with a superlong 10 nm inner diameter demonstrated the non-linear dependence of water permeability on inverse membrane thickness [21]. However, the systematic evaluation of the membrane structural parameter(s) (e.g. pore size, pore density, and membrane thickness) that are

important for the non-HP relationship of VA CNT membranes has not yet been performed. Thus, another objective of this study was to elucidate the parameter(s). To this end, the water permeabilities of all VA CNT membranes studied until now were compared using normalized forms based on the membrane pore structural parameters in the HP equation. Previously, the normalization of the measured water flux using the HP equation as flux enhancement was shown and compared with the results of a former study [20]. However, in this study, the water permeabilities of all results using VA CNT membranes were normalized using the HP equation, except for each pore structural parameter in the HP equation, and the main contributing parameter(s) to the abnormally fast water permeation through CNT holes was explored.

2. Materials and methods

2.1. Synthesis of VA CNTs

VA CNTs were synthesized following the protocol of Lee and Park [22]. The process was based on the water vapor assisted chemical vapor deposition (CVD) process. VA CNTs were grown on a SiO₂/Si wafer coated with aluminum (Sigma Aldrich, St. Louis, MO, USA) and iron (Sigma Aldrich) as catalyst layers. After the coating, the SiO₂/Si wafer was cut into rectangular chips with dimensions of 9 mm in width and 9 mm in length, and the chips were inserted into the cylindrical quartz reactor of the CVD machine. The carbon source was ethylene gas and its flow rate was 100 sccm (standard cubic centimeters per minute indicating cc/min at a standard temperature and pressure). The carrier gas was argon and its flow rate was 300 sccm. 200 sccm of hydrogen and 50 sccm of water vapor by argon purging was added to the main gas stream. Purged water was deionized (DI) water (humanpower I+, Human Corporation, Seoul, Korea). Until the reactor temperature was increased up to 750 °C, all gases, except for ethylene, traveled through the reactor and, after 40 min of heating, the carbon source began to flow to grow the CNTs. The reaction time was 30 min and the reactor was cooled in the air after the reaction.

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