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Water transport phenomena through membranes consisting of vertically-aligned double-walled carbon nanotube array

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ABSTRACT

Nanofluidics in CNTs is argumentative though it is theoretically calculated by various reports. It is because only a few of experimental reports are available, and the measured permeability is not so large as that suggested from the theoretical calculations. Also, water motion suppression in the confined space has not been exhibited by flux measurement. The present work explores these yet-unsolved discrepancies using the measurable size membrane of vertically aligned double-walled carbon nanotube array, which is borne with durability and flexibility, and a conventional measurement method is applied to the membranes. Water motion suppression occurs in the CNT confined space significantly, depending on temperature. Additionally, it is confirmed that the obtained permeability correlates to the reported experimental results with regard to the relationship between CNT length and permeability, and the correlation does not agree with permeability calculated from the Hagen-Poiseuille law. These results pose an insight into the inherent water transport characteristics in the CNT confined space.

1. Introduction

It has been proposed that the inner hollow spaces (confined spaces) of carbon nanotubes (CNTs) can be utilized for molecular separation of gas and liquid [1]. The study was originally initiated to explore characteristics of water in a confined space [2,3], and many theoretical ones have been reported [4–23]. The CNT confined space is of industrial interest because of the unique property [1]. A remarkable but phenomenological experimental result was also shown on proton transportation, concluding that CNT confined space behaved like artificial aquaporin [24]. Some of the assumptions for theoretical calculations have adopted the unrealistic boundary conditions on the state of confined water in CNTs, and they forecast ultra high flux through CNTs characteristically [5,6,8]. Those calculations have been hardly examined by experiment since it is subject to great restrictions on preparation and measurement in line with the hypotheses. Goh et al. elaborately discuss the current issues on nano carbon membranes in terms of the industrialization [25]. They pose the following points: concentration polarization, fouling, stability, scale up, and cost. Furthermore, the authors urge the necessity of standardization of the experimental methods to share the information.

Experimental evaluations of confined water in CNTs were conducted with observation of the water by transmission electron microscopy and the other methods [26]. As a result, the thermodynamic behaviors were obtained. At present, various measurement techniques for the confined water are proposed, however,

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they are conducted under the limited conditions [27–31]. There are two methods to measure the confined water in CNTs using gas and liquid, respectively. The former is adsorption of water molecules and the latter water permeability or flux measurement, respectively. Goh et al. consider the nanofluidics based on the Navie-Stokes equation suggesting no-gas hydrodynamics [32]. To investigate actual permeability of the confined water in CNTs, membranes consisting of vertically-aligned CNT array were developed aspiringly [33–37], however, they were still not sufficient for measuring actual permeability, nor standardized. After all, the consistency of the experimental results with the theoretical calculations has not been fully resolved yet. It has not also been examined which theoretical models are appropriate in describing the state of confined water in CNTs. As pointed out, any practical method has not been established to design an industrial membrane [25].

The present work aims to explore characteristics of the developed membrane consisting of Vertically-Aligned DWCNT (VA DWCNT) array, and to investigate the agreement between experimental results and the hypotheses for the theoretical calculations. A dead-end filtration apparatus that is one of the standard equipment to evaluate membrane performance for decades was used [38]. Both of the permeability and temperature dependence of flow are examined, where pure water is used to avoid the effect by the concentration polarization. The former seeks the effective slip-flow length and applicability of Hagen-Poiseuille law in the CNT confined space, which examines the correlation to the previous reports. The latter investigates water-freezing, or more precisely, water motion suppression in the confined space. It is noted that the suppression broadly includes structural formation of water. The early work on the confined water was started with a theoretical calculation of water behavior in the CNT confined space as mentioned above [2,3]. Those calculations adopted various assumptions and methods to obtain the conditions of confined water such as water models, interaction between water molecules and graphene surface, and CNT chirality. The calculations suggest that the flow velocity through CNTs is unusually high as 1000 times and more. However, the mechanical stability of those fabricated membranes was not discussed well, and many of them are made of brittle polymers or ceramics. The present work provides the membrane that is flexible and durable in large size to pursue reproducible measurement.

2. Experimental

2.1. Fabrication of membrane consisting of VA DWCNT array

The VA DWCNT array shown in Fig. 1 was prepared by a chemical vapor deposition (CVD) method using Black Magic II® (Aixtron SE, Germany). Typical synthetic methods for VA CNTs have been reported [39,40], and the details of procedure in the present work can be found elsewhere [41]. Fig. 2(A) schematically demonstrates the procedure of membrane fabrication. VA DWCNTs grow and form an array on a silicon wafer substrate from acetylene at 973 K under a nitrogen/hydrogen mixed atmosphere. The length of the DWCNTs was controlled to be 100 μm with an array density of approximately 2.8×10^{10} number-DWCNT/mm^2. The median outer diameter and distribution of the number of walls were 4.5 (Membrane 1) and 3.7 (Membrane 2) nm, and two layers, respectively, obtained from the transmission electron microscopy (TEM: JEM-2100F, JOEL Ltd., Japan) analysis of 100 samples each. The details are summarized in Fig. S1. The array on a silicon wafer substrate was placed in a vacuum deposition unit (PDS 2010, Specialty Coating Systems, Inc., United States), and was coated with parylene-C from the dimer (DPX-C, Specialty Coating Systems, Inc., United States). Parylene-C coating does not require any pretreatment of the DWCNT surface, which precludes any undesired surface change of CNTs. Details on parylene application and performance are discussed elsewhere [42–45]. The coated surface of the VA DWCNT array was manually milled, using an ultrafine polishing film of 0.30 μm particles (3 M® Lapping Film 261X). After milling, the VA DWCNT array membrane was peeled off from the substrate by a razor blade. The substrate-side surface was also milled in the same way to remove any lint after the peeling. The appearance of the membrane is shown in Fig. 3. Membrane thickness was measured with a micro figure measurement instrument (Surfcorder ET 200, Kosaka Laboratory Ltd., Japan).

The pore size distribution of the porous membranes was estimated by nanopermporometry [46]. In the case of nanopermporometry, where a mixture of a noncondensable gas and a condensable gas (vapor), is fed to the porous membranes, the permeability of the non-condensable gas is measured. The vapor is assumed to be capillary-condensed in membrane pores that are smaller than the following Kelvin diameter d_K, thus blocking the permeation of the non-condensable gas.

$$d_K = -4\nu\sigma\cos\theta/(RT\ln(P/P_s)) \quad (1)$$

where θ, σ, ν, P, and P_s are contact angle, surface tension, molar volume, vapor pressure, and saturation vapor pressure, respectively. The Kelvin diameter increases with the vapor pressure of a condensable gas in the feed. By measuring the permeability of the noncondensable gas as a function of relative pressure, P/P_s, it is possible to estimate the pore size distribution. A nano-perm porometer (Seika, Japan) was used for the measurements. In the present work, the noncondensable and condensable gases used were helium (He) and hexane (C_6H_{14}), respectively.

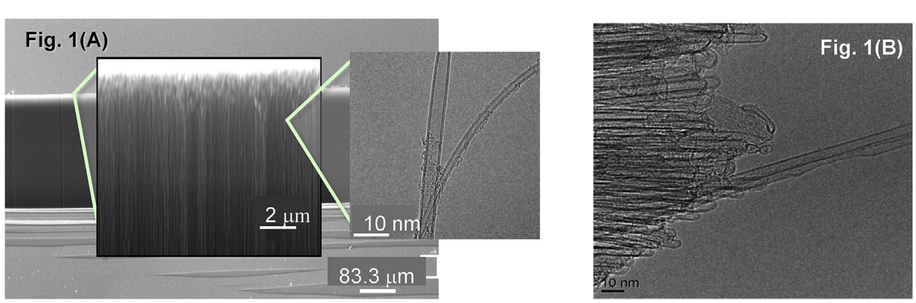

Fig. 1. Schematic SEM images of the vertically-aligned DWCNT (VA DWCNT) array. (A) DWCNTs grow as an array on a silicon wafer. The insets show the magnified upper section of the array and the VA DWCNTs. (B) TEM image of DWCNTs extracted from VA DWCNT array on substrate. The hollow structure of DWCNTs is clearly observed and it is different from the carbon nanofibers, which is known as Cup-Stacked CNTs. (A colour version of this figure can be viewed online.)