Carbon nanotube arrays hybrid membrane with excellent separation performance and conductivity

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ABSTRACT
Hybrid materials based on carbon nanotubes (CNTs) and polymers have shown attractive properties and potential applications. However, the poor quality and aggregation of CNTs are challenging during the preparation of hybrid materials. To address these issues, we fabricated the vertically aligned (VA) CNT (open-end) hybrid membrane with annealing treatment, which significantly improves the phenol separation performance, single gas permeability of CO₂ and N₂, and binary CO₂/N₂ mixture separation performance. The free volume provided by the orderly CNT channels and their atomically smooth walls contribute to the markedly increased diffusion rate and permeability of the membrane. The density functional theory (DFT) calculations indicate that the small molecules in the membrane preferentially transport along the internal channels of CNTs. Furthermore, this membrane also has excellent conductivity and resistance stability after 50 cycles of tensile deformation. For the first time, it reveals that this unique structured CNTs membrane can be applied in environmental, gas separation, and electronics fields with superior performance.

1. Introduction
Polydimethylsiloxane (PDMS) is a silicone elastomer from the synthetic polymer group. PDMS has the advantages of nontoxicity, flexibility, chemical inertness, thermal stability, and biocompatibility, which has been widely used in different fields, such as liquid separation, gas separation, and flexible electrodes [1–3]. However, it is well known that homogeneous PDMS membranes currently used for chemicals separation suffer from a trade-off between selectivity and permeability [4]. When used as conducting materials, homogeneous PDMS membranes exhibit poor conductivity and mechanical properties but excellent flexibility [1].

In order to overcome the limitations above, mixed-matrix membranes (MMMs) with inorganic/organic fillers are widely investigated [5]. Carbon nanotubes (CNTs) are excellent candidates with various advantages, such as outstanding mechanical properties, high strength-to-weight ratio, high specific surface area, and excellent conductivity [6,7]. Molecular dynamic (MD) simulations show that the flow rate of water in hydrophobic single-walled carbon nanotubes (SWCNTs) is five orders of magnitude faster than that of traditional materials, which is similar to that of aquaporin protein channel [8]. Skoulidas et al. have proved that, according to atomistic simulations, the transport of gases in CNTs is several orders of magnitude faster than that of zeolites [9]. Due to the large non-interacting van der Waals distance and an atomic-level smooth surface of CNTs, the inner wall of the CNT has a fast interfacial slip speed [10], thus endowing the CNTs with excellent liquid and gas transport performance. In recent years, CNTs/polymer composite membranes have been considered as a class of promising materials due to the combination of excellent properties of CNTs and polymers.

There has been a common challenge for a long time that random aggregation and disorder of CNTs in the polymer matrix result in the...
poor performance of CNTs/polymer composites in various applications \[11,12\]. The simulation by finite element method shows that the vertical alignment of CNTs can dramatically promote the transport of solute molecules along the CNTs direction \[13\]. When all the CNTs are completely perpendicular onto the film plane, molecules can transport through them with the fastest transfer rate. The ordered and parallel CNT arrays have considerable length, certain aspect ratio range, and consistent orientation \[14,15\]. The special structure endows CNT arrays with better performances than ordinary random CNTs \[16\]. Recently, a new type of membrane based on highly ordered CNTs has demonstrated extremely fast transport rate and excellent electrical conductivity \[17\]. Therefore, the aligned CNTs as effective reinforcing nanomaterials have great potential in polymers.

Chemical vapor deposition (CVD) is one of the common preparation methods for CNT arrays \[18\]. However, the prepared CNTs usually have metal catalyst nanoparticles, amorphous carbons, and structural defects \[19\], which seriously restrict their performances. High temperature annealing treatment has been proved to be a way to improve the purity and structural order of CNTs. According to Figarol et al. \[19\], high-temperature annealing treatment can significantly reduce the metallic impurities and structural defects in multi-walled CNTs (MWCNTs) \[20\]. In addition, Fiorito et al. confirmed that enhancing the crystallinity of MWCNTs can improve their electrical conductivity \[21\]. Therefore, treating the CNTs can change their properties and expand their potential applications.

In this work, we prepared and characterized the annealed VA CNT (open-end) hybrid membrane with multiple functions. The effects of structure and high temperature annealing treatment of CNTs on the phenol separation performance, single gas permeability of CO\(_2\) and N\(_2\), and binary CO\(_2\)/N\(_2\) mixture separation performance of hybrid membranes, and the mechanism for the different performances were studied. Through the density functional theory (DFT) calculations, we compared the relationship between the penetrant molecules and the adsorption energy of PDMS chain, CNT external wall, and CNT internal wall. In addition, the influence on the resistance stability of annealed VA CNT (open-end) hybrid membrane was also studied during stretching or twisting deformation.

2. Experimental

2.1. Materials

The Sylgared®184 silicone elastomer kit used in the preparation of PDMS membrane was purchased from Dow Corning Co., Ltd (Midland, Michigan, USA). Unaligned CNTs (Flotude 9000) powder was purchased from CNano Technology Co., Ltd (Santa Clara, CA, USA). The Si (100) substrates (3 cm × 3 cm) for CNT growth were purchased from Suzhou Crystal Silicon Electronics & Technology Co., Ltd (China). Ferrocene, xylene, n-pentane, hydrofluoric acid solution, and phenol were purchased from Damao Chemical Reagent Factory (China). N\(_2\), CO\(_2\), and He were purchased from Dalian GuangMing Special Gas Products Co., Ltd (China).

2.2. Preparation of membranes

The homogeneous PDMS membrane and the unaligned CNT (10 wt %) hybrid membrane were prepared by micron film applicator (Paul N. Gardner Company, USA). The detailed preparation method was described previously \[22\]. In brief, for PDMS homogeneous membrane, the base PDMS solution and curing agent were mixed in a proportion of 10:1, and a small amount of n-pentane was added as solvent. In the preparation of unaligned CNT (10 wt%) hybrid membrane, 10 wt% of CNTs and a proper amount of n-pentane were added into the PDMS mixed solution. The mixed solution was fully stirred. The mixture was evenly coated on the glass plate with a micron film applicator, and then placed in a vacuum oven at 80 °C for crosslinking reaction. Finally, the membrane was peeled from the glass plate.

The VA CNT (closed-end) hybrid membrane and the annealed VA CNT (open-end) hybrid membrane were fabricated according to our previous report \[16\]. In short, using xylene as the carbon source and ferrocene as the catalyst, VA CNT arrays were prepared by chemical vapor deposition (CVD). The prepared PDMS polymer solution was added to the CNT arrays drop by drop. The excess polymer at the top of the CNT arrays was removed by spin coating. The sample was placed in a vacuum oven at 80 °C for crosslinking reaction. Finally, the VA CNT (closed-end) hybrid membrane was prepared after stripped with hydrofluoric acid solution.

For the annealed VA CNT (open-end) hybrid membrane, the prepared CNT arrays were annealed at 1500 °C in Ar environment. The top of the CNT arrays was etched with Ar plasma by a low temperature plasma equipment. The prepared PDMS polymer solution was added to the CNT arrays drop by drop. The excess polymer at the top of the CNT arrays was removed by spin coating. The sample was placed in a vacuum oven at 80 °C for crosslinking reaction. The hybrid membrane was peeled off with hydrofluoric acid solution and turned over. The Ar/CF\(_4\) mixture plasma was used to etch the bottom of the hybrid membrane to open the CNTs at the bottom side. A thin layer of PDMS polymer was spin coated at the bottom of the hybrid membrane. Finally, the annealed VA CNT (open-end) hybrid membrane was prepared.

For the unannealed VA CNT (open-end) hybrid membrane, except that the VA CNT arrays did not undergo high temperature annealing treatment, the remaining preparation process was the same as that of the annealed VA CNT (open-end) hybrid membrane. The thickness of the five membranes is almost the same (ca. 70 μm).

2.3. Materials characterisation

The surface and cross-sectional morphology of the materials were characterized by scanning electron microscope (SEM, QUANTA 450), transmission electron microscopy (TEM, FEI Tecnai G2 Spirit), and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F30S-Twin). The crystalline phases of VA CNT arrays were examined using Rigaku D/MAX-2400 diffractometer (XRD) equipped with a rotating anode and a CuK\(_\alpha\) radiation source (λ = 0.15418 nm). The functional groups of PDMS and annealed VA CNT (open-end) hybrid membrane were analyzed with Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 Flex, Thermo Fisher Scientific) in attenuated total reflectance (ATR) mode. The phenol titer (OD269) was measured with a rotating anode and a CuK\(_\alpha\) radiation source.

2.4. Pervaporation (PV) experiment

The PV experiments with 15 g/L phenol aqueous solution as feed were carried out using five kinds of membranes, and the methods were similar to those in the previous study \[16\]. The detailed methods are shown in the Supplementary material S1.

The flux (\(J\), g/m\(^2\)h), separation factor (\(\alpha\)), and Pervaporation Separation Index (PSI) were calculated as follows:

\[
J = \frac{w}{A t} \quad (1)
\]

\[
\alpha = \frac{y/(1-y)}{x/(1-x)} \quad (2)
\]

\[
PSI = J \alpha \quad (3)
\]

where \(W\) is the weight of the recovered permeate in gram, \(A\) is the membrane area in m\(^2\), and \(t\) is the time (h) for the sample collection. \(x\) and \(y\) are the weight fractions of components in the feed and permeate.
samples, respectively.

2.5. Models and calculation method

The detailed method of DFT simulation and the calculation formula of adsorption energy ($E_a$) were described in the previous work [16]. DMOL3 package was used to perform all calculations. The generalized gradient approximation PW91 was used to describe the exchange-correlation interactions. A double numerical basis set plus d-polarization function (DNP) was employed as implemented in the DMOL package. The OBS DFT-D method was used to consider the van der Waals interaction. The interaction between adsorbate and substrate was modeled by a single-walled armchair (7, 7) nanotube. PDMS was modeled by four repeating monomer [SiO(CH$_3$)$_2$] units. The interaction energy ($E_b$) was calculated by the energy difference between interaction complex ($E_{adsorbate + substrate}$) and adsorbate ($E_{adsorbate}$) and substrate ($E_{substrate}$).

2.6. Measurement of gas permeation and separation performance

The gas permeation and separation performance of five kinds of membranes were tested by a gas permeation apparatus from Dalian ZhongjiaruiLi Liquid Technology Co., Ltd (China). The calculation methods of related parameters (gas permeability coefficient ($P_i$, Barrer); selectivity of a gas pair ($a_{ij}$)) were the same as those previously reported [23,24]. The detailed methods are shown in the Supplementary material S2.

The gas permeability coefficients and selectivity were calculated with the following equations:

$$P_i = \frac{q_i L}{A \Delta P_i}$$  \hspace{1cm} (4)

$$a_{ij} = \frac{P_i}{P_j}$$  \hspace{1cm} (5)

Fig. 1. Characterization of VA CNT arrays and annealed VA CNT (open-end) hybrid membrane. (a) SEM image by side view of VA CNT arrays at low magnification; (b) SEM image by side view of VA CNT arrays at high magnification; (c) HR-TEM image showing the multilayered structure of a single MWCNT (inset: typical (002) electron diffraction spots observed in a microdiffraction pattern); (d) TEM image of CNT ends after Ar etching; (e) SEM image of the internal cross-sectional of the membrane; (f) TEM image of the cross-sectional of the membrane; (g) XRD pattern of VA CNT arrays; (h) ATR-FTIR spectra of homogeneous PDMS membrane and annealed VA CNT (open-end) hybrid membrane.
where $P_i$ is the gas permeability coefficient, Barrer (1 Barrer $= 10^{-10}$ cm$^2$(STP) cm/(cm$^2$ s cmHg)), $q_i$ is the gas permeation flux of component $i$, m$^3$. $t$ is the time for gas permeation, s. $\Delta p_i$ is the partial pressure difference of component $i$, Pa. $L$ is the membrane thickness, m. $A$ is the membrane area available for gas transport, m$^2$. $\alpha_{ij}$ is the selectivity of gas pair $i/j$.

### 2.7. Measurement of electrical conductivity

The two ends of the membranes were connected with a wire through conductive silver adhesive. The two ends of the wire were connected with the electrochemical workstation to form a conductive path. The tensile deformation and release process of the membranes were controlled by a pull-up instrument. Thus, the current variation of the membranes could be obtained simultaneously with the membrane strain. Electromechanical property was recorded by a CHI660E electrochemical workstation.

The resistance ($R$) and volume resistivity ($\rho$, $\Omega$-m) were calculated from the characteristic $I$-$V$ curves by taking into account the geometrical characteristics of the sample, using the following equations:

$$R = \frac{V}{I}$$  \hspace{1cm} (6)

$$\rho = \frac{V \times A}{I \times L}$$  \hspace{1cm} (7)

where $V$ is the applied voltage. $I$ is the measured current. $A$ is the cross-sectional area of the electrodes. $L$ is the distance between electrodes.

Electrical conductivity ($\sigma$, S/m) was then calculated as the inverse of the resistivity ($\rho$):

$$\sigma = \frac{1}{\rho}$$  \hspace{1cm} (8)

### 3. Results and discussion

#### 3.1. Characterisation of CNTs and the annealed VA CNT (open-end) hybrid membrane

As shown in Fig. 1(a), the CNTs are highly aligned and continued from the bottom to the top in the arrays (ca. 65 $\mu$m). It is clear from Fig. 1(b) that the adjacent CNTs are highly aligned. The HR-TEM image (Fig. 1(c)) indicates that the prepared CNT after high temperature annealing treatment is hollow tubular. The microdiffraction pattern obtained from a single CNT shows the existence of (002) reflections, confirming the highly ordered structure (inset in Fig. 1(c)). Fig. 1(d) shows that the plasma etching process can successfully open the CNT end. SEM image of the internal cross-section of the annealed VA CNT (open-end) hybrid membrane (Fig. 1(e)) shows that CNTs are uniformly distributed in PDMS polymer. PDMS is well filled entre CNTs gaps with excellent compatibility, forming a defect-free hybrid membrane structure. TEM image from the cross-sectional view of the membrane (Fig. 1(f)) further verifies that CNTs keep a vertically aligned structure and are adequately dispersed in PDMS.

From the XRD pattern of CNTs in Fig. 1(g), it can be seen that there are two characteristic peaks. There is a strong (002) diffraction peak at 26° and a weak (100) diffraction peak at 42.8°. The chemical structures of PDMS membrane and annealed VA CNT (open-end) hybrid membrane are characterized by ATR-FTIR (Fig. 1(h)). The peaks at 2963 and 2903 cm$^{-1}$ result from the stretching vibration of C-H in Si-(CH$_3$)$_2$. The peak at 1253 cm$^{-1}$ shows the variable angle vibration of Si and two –CH$_3$. The broad and shouldered peaks at 1060 and 1007 cm$^{-1}$ indicate the stretching vibration of Si-O-Si. The peak at 843 cm$^{-1}$ shows the stretching vibration of Si-C. The strong peak at 787 cm$^{-1}$ verifies the plane rocking vibration of –CH$_2$ in Si-(CH$_3$)$_2$. Compared with the spectrum of homogeneous PDMS membrane, there is no new characteristic peak in the spectrum of annealed VA CNT (open-end) hybrid membrane, which indicates that there is no chemical reaction between CNTs and PDMS polymer matrix, only physical blending.

#### 3.2. PV performance for phenol recovery

Here, since the separation of phenolic substances from industrial wastewater streams is of great importance from an environmental perspective, we investigated the PV separation performance of the membranes to recover phenol from water (Fig. 2(a–d)). The PV system is illustrated in Fig. 2(e). Compared with those of the homogeneous PDMS membrane, the total flux, phenol flux, and separation factor are moderately improved with the unaligned CNT hybrid membrane. Molecular dynamic (MD) simulation shows that the molecules diffuse by “jumping” between the cavities in the polymer matrix [25,26], resulting in...
in low diffusion coefficient (Fig. 3(a)). After random/disordered CNTs are filled into PDMS polymer, CNTs provide irregular transportation routes for the diffusion of molecules, which can diffuse along the smooth and hydrophobic CNTs surface, resulting in moderate enhancement in the recovery of phenol from water. Nevertheless, the random CNTs tend to self-aggregate due to their strong van der Waals and π-π interactions [27, 28], which thus hinders the separation performance of phenol in the unaligned CNT hybrid membrane (Fig. 3(b)).

As shown in Fig. 2(a–d), the VA CNT (closed-end) hybrid membrane has a higher total flux, phenol flux, and separation factor of 141.4 g/m²·h, 28.5 g/m²·h, 16.7, respectively, increasing by 49.2%, 114.1%, and 54.7% compared to those of unaligned CNT hybrid membrane. The CNT film without anisotropic structures can exhibit superhydrophobic property due to the vertically aligned structure and the significant air trapping [29]. Moreover, the VA CNT (closed-end) hybrid membrane can present a higher flux, since the orderly distributed CNTs can be filled with a larger mass fraction [16] and allow the molecules to transport along the CNTs wall (Fig. 3(c)).

Compared with the VA CNT (closed-end) hybrid membrane, the total flux (211.9 g/m²·h) and phenol flux (39.4 g/m²·h) of the unannealed VA CNT (open-end) hybrid membrane are further increased, but the separation factor (15.0) is slightly decreased (Fig. 2(a–d)). Once both ends of the CNTs are opened, the unannealed VA CNT (open-end) hybrid membrane can form internal nano-channels (ca. 10 nm), facilitating the molecules (e.g., water and phenol) (Table 1) to diffuse through the membrane (Fig. 3(d)). However, because the CNT arrays have not been annealed at high temperature, there are metallic catalyst nanoparticles and amorphous carbon in the prepared CNTs, which can block the transportation channels of CNTs, leading to limited improvement in the separation performance of the unannealed VA CNT (open-end) hybrid membrane.

To be highlighted, the annealed VA CNT (open-end) hybrid membrane has the highest total flux and phenol flux of 322.9 g/m²·h and 56.2 g/m²·h, respectively. After the CNT arrays are annealed at high temperature, the open-ended CNTs and smooth CNT graphite sheets offer better transport channels for small molecules in the annealed VA CNT (open-end) hybrid membrane (Fig. 3(e)), which remarkably enhances the diffusion rate of the small molecules. In addition, since the diameter of the water molecule is smaller than that of the phenol molecule (Table 1), the diffusion rate of the water molecule is faster than that of the phenol molecule, resulting in a decrease in the separation factor. More importantly, the PSI values of the annealed VA CNT (open-end) hybrid membrane are significantly higher than those of other membranes, indicating that the annealed VA CNT (open-end) hybrid membrane has an unexpectedly high separation performance.

Table 2 lists the phenol pervaporation performances of different types of membranes. As shown in Table 2, the phenol separation performances of annealed VA CNT (open-end) hybrid membrane prepared

---

Table 1

<table>
<thead>
<tr>
<th>Molecular</th>
<th>Diameter (Å)</th>
<th>Solubility parameter (MPa)¹/²</th>
<th>δₐ</th>
<th>δₚ</th>
<th>δₜ</th>
<th>δ(SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water [16]</td>
<td>2.7</td>
<td>18.0</td>
<td>28.0</td>
<td>54.0</td>
<td>47.8</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>6.2</td>
<td>15.0</td>
<td>15.0</td>
<td>29.0</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>PDMS [16]</td>
<td></td>
<td>15.9</td>
<td>0.1</td>
<td>4.7</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>3.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>3.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>


Table 2

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Feed (wt%)</th>
<th>Temperature (°C)</th>
<th>Total flux (g/m²·h)</th>
<th>Separation factor</th>
<th>PSI</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>0.5</td>
<td>60</td>
<td>420</td>
<td>2.2</td>
<td>924</td>
<td>[30]</td>
</tr>
<tr>
<td>OA-PDMS</td>
<td>0.5</td>
<td>40</td>
<td>110</td>
<td>2</td>
<td>220</td>
<td>[30]</td>
</tr>
<tr>
<td>PIM-1</td>
<td>1</td>
<td>70</td>
<td>210</td>
<td>16</td>
<td>3360</td>
<td>[31]</td>
</tr>
<tr>
<td>PEBA/PU</td>
<td>0.1</td>
<td>35</td>
<td>84.1</td>
<td>9.7</td>
<td>815.77</td>
<td>[32]</td>
</tr>
<tr>
<td>MWCNTs/PU</td>
<td>0.5</td>
<td>80</td>
<td>175.6</td>
<td>2.8</td>
<td>491.68</td>
<td>[33]</td>
</tr>
<tr>
<td>SiO₂/PDMS/PVDF</td>
<td>0.001</td>
<td>80</td>
<td>1585</td>
<td>4.56</td>
<td>72227.6</td>
<td>[34]</td>
</tr>
<tr>
<td>Annealed VA CNT (open-end)/PDMS</td>
<td>1.5</td>
<td>37</td>
<td>322.9</td>
<td>13.9</td>
<td>5019.3</td>
<td>This work</td>
</tr>
</tbody>
</table>
in this work are higher than those of various membranes reported in the literature [30–33]. Although the ZSM-5/PDMS/PVDF membrane and the C-CNT-OH/PU membrane have higher fluxes, they exhibit lower separation factors with higher operating temperatures [34, 35], which are not suitable for industrial applications. Therefore, the annealed VA CNT (open-ended) hybrid membranes show potential in the separation of phenolic or aromatic compounds in industrial wastewater.

3.3. Gas permeation and separation performance

To further explore the potential application of gas separation, we compared the single gas permeability of CO₂ and N₂ and the binary CO₂/N₂ mixture separation performance using five types of membranes (Fig. 4(a–c)) with He as the sweep gas. The close-circulating gas permeability system is illustrated in Fig. 4(d). As shown in Fig. 4(a and b), the overall CO₂ permeability is much higher than N₂ due to its strong adsorption, plasticization and good solubility [36]. Moreover, the kinetic diameter of CO₂ is smaller than N₂ (Table 1) and thus CO₂ diffuses more easily in the membrane. For the single gas permeability, the permeability for CO₂ and N₂ and the calculated CO₂/N₂ ideal selectivity gradually increase (Fig. 4(a–c)). Among these membranes, the annealed VA CNT (open-end) hybrid membrane demonstrates the best separation performance, showing the CO₂ and N₂ permeability of 7401 Barrers and 346 Barrers, respectively, and the CO₂/N₂ selectivity of 21.4 at 25 °C and 0.1 MPa. For the binary CO₂/N₂ mixture separation performance, the permeability for CO₂ and N₂ in equimolar CO₂/N₂ mixture as well as the CO₂/N₂ mixture selectivity also gradually increases (Fig. 4(a–c)). However, due to the competitive adsorption in gas mixture separation, the gas permeability and selectivity in gas mixture separation are slightly lower than those in single component gas separation. The annealed VA CNT (open-end) hybrid membrane also has the best separation performance among these membranes, with the permeability of 6836 Barrers and 337.5 Barrers for CO₂ and N₂, respectively, and the selectivity of 20.3 for CO₂/N₂ mixture. In a word, the open-ended CNT arrays play a significant role in facilitating the transport of gas molecules in the membrane.

In general, there are three mechanisms (Knudsen diffusion, viscous flow, and surface flow) for pure gas transport through porous membranes [37]. Knudsen diffusion occurs when the mean free path (λ) of gas molecules is larger than the pore radius (r) of the membrane. In the Knudsen diffusion process, the main event is the collision between gas molecules and the pore wall, not the collision between gas molecules. The λ for most gas molecules at room temperature is significantly larger compared to the radius of the transport channel in the CNT. For example, the λ of air at room temperature is ~600 Å, which is an order of magnitude larger than the inner diameter of CNT we prepared. Therefore, theoretically Knudsen diffusion occurs in the CNT transport channels of the annealed VA CNT (open-end) hybrid membrane. In addition, due to the smooth atomic surface in the CNT channel, the collision property between the gas and the tube wall changes from purely diffuse in the Knudsen model to a combination of diffuse and specular collisions [38], thus accelerating the diffusion speed of gas molecules in the CNT channel. These theoretical predictions have been verified in CNT dynamic theoretical simulation and experiments [39, 40]. Therefore, filling high-quality hollow CNT arrays with open ends into PDMS polymer significantly improve the gas permeability of hybrid membrane. The annealed VA CNT (open-end) hybrid membrane with outstanding gas permeation performance has promising applications in CO₂ capture or other gas separation processes.

3.4. DFT calculations

The combination of adsorption and diffusion characteristics of gas or liquid molecules penetrating into the membrane determines the
permeability and selectivity of the separation membrane. Understanding the mechanism underlying the adsorption of molecules onto the CNT and PDMS chain is of great importance to further investigate the open-ended CNT arrays for the improvement of the membrane performance. By means of DFT calculations, we investigated the adsorption of various molecules (C₆H₅OH, N₂, and CO₂) onto the PDMS chain and the internal and external walls of CNT. The main interactions in these molecule-adsorbing systems are physical adsorption, and the adsorption energy values of various molecules are shown in Table 3. The optimized structures of typical adsorbed molecules (C₆H₅OH, N₂, and CO₂) onto the PDMS chain, the internal and external walls of the CNT are shown in Fig. 5.

According to Table 3, the adsorption energy of phenol (C₆H₅OH) with PDMS chain and CNT is greater than that of H₂O. Therefore, PDMS and CNT preferentially adsorb phenol molecules in phenol aqueous solution. The result is the same as that predicted by Hansen solubility parameters (Table 1). The adsorption energy of H₂O with the PDMS chain is larger than that with the external and internal wall of CNT (Table 3), which indicates that CNT is more hydrophobic compared to PDMS. In addition, the adsorption energy of C₆H₅OH with PDMS chain is greater than that with the external wall of CNT, which proves that PDMS has higher selectivity to C₆H₅OH than the external wall of CNT. That is, when phenol molecules and water molecules penetrate into the unaligned CNT hybrid membrane and the VA CNT (closed-end) hybrid membrane, PDMS chain will preferentially adsorb phenol molecules and water molecules compared with the external wall of CNT. However, due to the “jump” diffusion mechanism and the limited free volume in PDMS polymer, the diffusion rate of water molecules and phenol molecules in PDMS polymer is relatively low [25]. Although the adsorption energy of C₆H₅OH and H₂O with the external wall of CNT is lower, the diffusion rate of the external wall of CNT is higher than that with PDMS polymer.

Table 3
Summary of adsorption distance (d) and adsorption energy (Eₐ) of different molecules on different adsorption sites calculated from DFT simulations.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>PDMS chain</th>
<th>External wall of CNT</th>
<th>Internal wall of CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d (Å)</td>
<td>Eₐ (kJ/mol)</td>
<td>d (Å)</td>
</tr>
<tr>
<td>H₂O [16]</td>
<td>2.10</td>
<td>–61.5</td>
<td>3.27</td>
</tr>
<tr>
<td>C₆H₅OH</td>
<td>2.46</td>
<td>–81.0</td>
<td>3.11</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.01</td>
<td>–14.8</td>
<td>3.05</td>
</tr>
</tbody>
</table>

Fig. 5. Optimized structure of molecules on the PDMS chain and on the external and internal wall of CNT: (a–c) phenol; (d–f) CO₂; (g–i) N₂.
due to the large specific surface area and the smooth surface of the external wall of CNT. Therefore, filling the closed-end CNTs into PDMS polymer can increase the flux of the hybrid membrane. What’s even more remarkable is that the adsorption energy of C\textsubscript{2}H\textsubscript{5}OH with the internal wall of CNT is greater than that with the PDMS chain and the external wall of CNT. Accordingly, when phenol molecules penetrate into the annealed VA CNT (open-end) hybrid membrane, phenol molecules will be preferentially adsorbed onto the internal wall of CNT. For polymers with different structures, the diffusion coefficient of solute molecules in the polymer is relevant to the free volume fraction of the polymer [41]. In the annealed VA CNT (open-end) hybrid membrane, the hollow tubular channels of the open-ended CNTs as permeable inorganic phase significantly increase the free volume of the hybrid membrane (Fig. 3(e)), making the diffusion coefficient of the annealed VA CNT (open-end) hybrid membrane larger than the other four membranes of the control group. Therefore, the flux of the annealed VA CNT (open-end) hybrid membrane is significantly higher than that of the other four membranes in the control group.

For gas molecules, the adsorption energies of CO\textsubscript{2} with PDMS chain and CNT are larger than those of N\textsubscript{2} (Table 3). Furthermore, the kinetic diameter of CO\textsubscript{2} is smaller than N\textsubscript{2}. Therefore, CO\textsubscript{2} is more easily adsorbed and transported onto PDMS chain and CNT than N\textsubscript{2}, which is in excellent agreement with our demonstrating results and other studies [42,43]. In addition, the adsorption energies of the CO\textsubscript{2} and N\textsubscript{2} onto the internal wall of CNT are larger than those onto the external wall of CNT and the PDMS chain. Consequently, the internal wall of CNT for gas adsorption is more favorable than the external wall of CNT and the PDMS chain. Additionally, according to the results predicted by dynamics simulation and calculation, the diffusion rate of gas in the CNT channel is several orders of magnitude faster than that of other materials [44,45]. Hence, the rapid diffusive transport in CNTs along with their adsorption property enables the annealed VA CNT (open-end) hybrid membrane to exhibit extremely high permeability.

### 3.5. Stretchable conductor based on VA CNT arrays

Stretchable conductors have superior mechanical properties compared to traditional rigid conductors, and showed good application prospects in the fields of deformable displays and flexible sensors [46,47]. The aligned CNT/PDMS hybrid membrane may represent a new family of stretchable conductors which overcomes the challenge of randomly dispersed CNT/PDMS membrane [48].

As shown in Table 4, the resistivity of the annealed VA CNT (open-end) hybrid membrane is significantly lower than those of the homogeneous PDMS membrane and unaligned CNT hybrid membrane (eight and four orders of magnitude lower, respectively). In contrast, the conductivity of the annealed VA CNT (open-end) hybrid membrane is dramatically higher than that of the homogeneous PDMS membrane and unaligned CNT hybrid membrane (eight and four orders of magnitude higher, respectively). Since the VA CNT arrays in PDMS polymer matrix form a three-dimensionally interconnected network, which can be seen in the SEM images (Fig. 1(e)), the composite membrane is electrically conductive in all directions. Therefore, the high conductivity of the annealed VA CNT (open-end) hybrid membrane is mainly attributed to the highly ordered CNT arrays and high loading of CNTs in PDMS polymer matrix.

Moreover, in order to investigate its stretchability as a conductor, we measured the electrical resistances of the annealed VA CNT (open-end) hybrid membrane in the two states during the deforming processes. Hereafter we refer to the initial resistance of the annealed VA CNT (open-end) hybrid membrane with zero strain as \(R_0\). Fig. 6(a and b) compares the normalized resistances \((R/R_0)\) of the annealed VA CNT (open-end) hybrid membrane under the tensile strain of 0%, 30%, 50%, and 70% in the normal state. The resistances are nearly unchanged (<3%) during the stretching process. Furthermore, after 50 cycles of stretching, the resistances are almost the same (Fig. 7(a)), and the drift of \(R/R_0\) is less than 1%. Similarly, nearly no resistance changes (<5%) are exhibited when the tensile strain of the annealed VA CNT (open-end) hybrid membrane is 0%, 30%, 50%, and 70% in the twist 180° state.

**Table 4**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Resistivity ((\rho, \Omega \cdot \text{m}))</th>
<th>Conductivity ((\sigma, \text{S/m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>(1.23 \times 10^6 (\pm 0.04 \times 10^6))</td>
<td>(8.14 \times 10^{-7} (\pm 0.27 \times 10^{-7}))</td>
</tr>
<tr>
<td>Unaligned CNT/PDMS</td>
<td>(1.18 \times 10^6 (\pm 0.03 \times 10^6))</td>
<td>(8.48 \times 10^{-5} (\pm 0.22 \times 10^{-5}))</td>
</tr>
<tr>
<td>VA CNT (closed-end)/PDMS</td>
<td>(7.50 \times 10^{-2} (\pm 0.02 \times 10^{-2}))</td>
<td>(13.34 (\pm 0.04))</td>
</tr>
<tr>
<td>Unannealed VA CNT (open-end)/PDMS</td>
<td>(5.68 \times 10^{-2} (\pm 0.03 \times 10^{-2}))</td>
<td>(17.61 (\pm 0.10))</td>
</tr>
<tr>
<td>Annealed VA CNT (open-end)/PDMS</td>
<td>(2.16 \times 10^{-2} (\pm 0.06 \times 10^{-2}))</td>
<td>(46.30 (\pm 0.43))</td>
</tr>
</tbody>
</table>

**Fig. 6.** (a) In the normal state, the images of the annealed VA CNT (open-end) hybrid membrane under tensile strain of 0%, 30%, 50%, and 70%; (b) in the normal state, dependence of normalized resistance \((R/R_0)\) of the membrane on the strain of elongation. \(R_0\) and \(R\) correspond to electrical resistances of the membrane before and after deformation. (c) In the twist 180° state, the images of the annealed VA CNT (open-end) hybrid membrane under tensile strain of 0%, 30%, 50%, and 70%; (d) in the twist 180° state, dependence of normalized resistance \((R/R_0)\) of the membrane on the strain of elongation.
Fig. 7. Dependence of normalized resistance ($R/R_0$) on the number of stretch-release cycles: (a) in the normal state; (b) in the twist 180° state.

Fig. 8. A diagram showing stretching and recovery of the accordion structure of a conducting CNT forest network embedded into PDMS matrix.
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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