Atomic layer deposition of metal oxides on carbon nanotube fabrics for robust, hydrophilic ultrafiltration membranes

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ABSTRACT

Carbon nanotubes (CNTs) are important building blocks to produce high-performance membranes. However, the strong hydrophobicity significantly hinders their applications in aqueous systems. Herein, we demonstrate, for the first time, that atomic layer deposition (ALD) is an efficient and flexible method to upgrade the permeability of CNT-based membranes. We ALD-deposit ZnO on fabrics of multi-walled carbon nanotubes. ZnO grows on the CNT surface as nanoparticulates initially and then forms conformal layers wrapping the CNTs. The originally hydrophobic surface of CNTs is progressively turned to be highly hydrophilic with rising ALD cycles. The deposition of ZnO on CNTs significantly promotes the surface wettability of the CNT membranes on one hand, and endows the membrane an enhanced mechanical stability on the other. The CNT membranes exhibit simultaneously upgraded water permeability and retention in the ultrafiltration category after ALD for moderate cycle numbers. With ever increased ALD cycles, the retention is further improved while the water permeability is decreased due to the competing effect of the increased hydrophilicity and narrowed pores. The strategy of “ALD on CNT substrates” is expected to produce other robust membranes with additional functionalities dependent on the materials to be deposited by ALD.

1. Introduction

Due to their uniform, nanometer-sized diameters with extremely large aspect ratios, narrow channel-like interiors, and exceptional mechanical, thermal, and chemical stabilities, carbon nanotubes (CNTs) have become a type of very interesting and promising building blocks for advanced membranes [1,2]. A number of strategies have emerged to use CNTs in the preparation of different membranes, and these strategies can be roughly divided into three groups. The most striking strategy is to vertically align CNTs in polymer matrices and fluid flow is confined to take place only through the interior hollow CNTs [3,4]. The aligned CNT membranes exhibit a water flux several times larger than that of common UF membranes. Moreover, they also exhibit greater resistance to biofouling as a result of significant reduced bacterial attachment [5]. Although many modeling studies have demonstrated the exceptional water permeabilities of these aligned CNT membranes [6,7], so far there are very few experimental reports on the real preparation of these membranes with comparable permeabilities to the theoretical predictions. This is because of the tremendous challenges in vertical alignment of CNTs in the polymer matrix as well as the inhomogeneous chemistry and physical spaces of CNTs. As a result, this strategy is far from upscaling and real applications.

Incorporating CNTs into the membrane matrices as fillers is the most convenient way to prepare membranes with enhanced mechanical strength or water permeabilities [8–12]. In this strategy, CNTs are dosed into the polymer constituents and present in the final membranes with random orientation. Their hollow interiors, in most cases, are not accessible to water, and therefore, do not contribute to water permeance. Instead, the interfaces between the CNTs and the polymer matrix are believed to provide additional porosities to allow water flow. Consequently, enhanced water permeabilities are achieved. However, to have a good dispersion in thick polymer matrix, CNTs are typically required to be chemically modified to enhance the compatibility with the polymers [13], which is usually time- and energy-consuming and tedious process.

Alternatively, randomly entangled CNTs in the form of fabrics can be directly used as free-standing membranes [14–16]. The main advantage of this type CNT membranes is their three-dimensionally (3D) interconnected nanoporous networks with high specific surface areas. The pores of the free-standing CNT membranes are defined by the gaps...
of neighboring CNTs, and the pore sizes are predominantly determined by the diameter of the CNTs. Because the diameter can be as small as a few nanometers for single-walled CNTs, this type of CNT membranes possess great flexibility to tune their pore sizes approaching the nanofiltration category simply by using thin tubes [17]. Thanks to their excellent mechanical, thermal, and electronic properties, free-standing CNT fabrics have been used in diverse applications [18–21]. However, very limited studies are focused on the membrane separation performances of the free-standing CNT used to modify or to functionalize CNT-based separation membranes. The first reason is weak connections between individual CNTs. Enhancing the mechanical properties of the CNT fabrics is important because it lowers the risks of release individual CNTs into the environment [22]. Some studies have revealed that CNTs may pose serious security issues when exposed to air or water [23,24]. This risk can potentially be eliminated by welding the nanotubes with each other in free-standing CNT fabrics, for example, via surface coating.

For applications in aqueous systems, the inherent strong hydrophobicity of CNTs is another big problem, which reduces water permeability and causes membrane fouling. A number of works have been reported to improve the hydrophilicity of CNTs. Functionalization has been done to generate polar groups on CNTs, thus enhancing the wettability of the CNT fabrics [25–27]. Through such functionalization the CNT-based membranes show increased water flux and selective rejection of pollutant. CNTs can also be decorated with various nanoparticles such as metals, polymers, and biomolecules which not only offer additional attractive properties but also enhance the water affinity of the CNT membranes [27].

The functionalization and modification of CNT membranes needs to be precisely controlled. Therefore, there is a strong need for highly controllable methods which allow the modification of CNT membranes in a simple way. Atomic layer deposition (ALD), based on self-terminating surface reactions, is an efficient technique to depositing thin films conformally on various substrates, which could control the deposited material amount with superb precision and down to atomic level. The nucleation and growth of metal oxides during the ALD process on a variety of polymeric substrates have been intensively investigated in recent years and confirm the good adaptability of ALD technique [28]. While the slow deposition rate, low-throughput and high-cost ensues with the excellent film quality control, which are the challenges impeding the ALD to scale-up. However, the ALD could achieve continuous production by using batch processing or spatial reacting methods to scale-up [29–32]. In ALD the material to be deposited is synthesized directly on the substrate surface instead of being deposited from the vapor phase as in other thin film deposition techniques. Because of this surface-driven process, ALD is capable of building conformal coatings over substrates with complex geometries and also porous media [33]. By leveraging the extreme precision in the thickness control as well as the high infiltrability of the vaporized precursors of ALD, we demonstrated the capability and flexibility of ALD to deposit metal oxides in the pore walls for precisely tuning pore sizes, surface properties and the separation properties of a number of porous membranes [34–39]. ALD of thin films and nanoparticulates on CNTs has been realized for several oxides and metals, such as Al2O3, TiO2, ZnO, and V2O5 [40–43]. However, until now ALD has never been used to modify or to functionalize CNT-based separation membranes.

In present study, we focus on improving the hydrophilicity, structural stability and separation performances of the free-standing CNT fabrics by ALD, then using them as robust and hydrophilic ultrafiltration membranes. The amount and surface coverage of CNTs with ZnO nanoparticulates were controlled by the ALD reaction cycles. Significant improvement in structural stability and water wettability were achieved by ALD of ZnO on the CNT fabrics. More importantly, the water permeability and separation performance were greatly improved at the same time when the CNT fabrics were deposited with moderate ALD cycles. This work opens a new avenue to upgrade the performances of CNT membranes on one hand, and provide the possibility to offer additional functionalities to the CNT membranes depending on the materials to be deposited by ALD.

2. Experimental

2.1. Materials

Sheets of multi-walled CNT fabrics with a thickness of ~8 μm were purchased from Suzhou Jiedi Nanotechnology Co., Ltd. Diethyl zinc (DEZ) with a purity of 99.99% (Nanjing University) and deionized water with a conductivity of 8–20 μs/cm (Wahaha Co., Ltd.) were used as the precursors for the ALD of ZnO. Anhydrous ethanol and hydrochloric acid were obtained from local suppliers. Bovine serum albumin (BSA) was ordered from Sigma-Aldrich and dissolved in phosphate buffer solutions (PBS) for retention tests.

2.2. ALD of ZnO on Si wafers and CNT fabrics

The pristine CNT fabrics were cut into discs with a diameter of 2.5 cm. To remove surface impurities, the CNT discs were then soaked in 20% hydrochloric acid for 3 days, followed by washing with deionized water, and finally dried at 100 °C. ALD of ZnO on Si wafers and the cleaned CNT discs was simultaneously carried out in the f-100-31 ALD reactor from Wuxi MNT Micro and Nanotech Co., Ltd. The Si wafers and CNT fabrics were positioned in the ALD chamber. The chamber was heated to 150 °C and maintained at this temperature for 1 h under vacuum (~133 Pa) before deposition. Ultrahigh purity nitrogen (99.999%) and high purity nitrogen (99.9%) were used as the carrier gas and purge gas during the ALD process, respectively. One typical ALD cycle consisted of pulse, exposure, and purge for each precursor. DEZ and deionized water vapors were alternatively pulsed into the ALD chamber by the carrier gas. The pulse duration of DEZ and water was 0.075 s and 0.05 s, respectively. After pulse, each precursor was held in the chamber for 10 s, allowing the substrates to be sufficiently exposed in the precursor vapors. Nitrogen was subsequently purged into the chamber at a flow rate of 20 sccm for 60 s to sweep the unreacted precursors and byproducts out. CNT fabrics were deposited for 20, 40, 60, 80, and 100 cycles, respectively.

2.3. Characterizations

Scanning electron microscopy (SEM) investigations of the samples were performed on a Hitachi S4800 microscope operated at 5 kV to observe the surface and cross-sectional morphologies. Because of the excellent conductivity of CNTs, all the samples were directly observed by SEM without a sputter-coating of metals. An FEI Tecnai G2 F30 S-Twin transmission electron microscope (TEM) operated at 300 kV was used to probe the microstructures of the ZnO-deposited CNTs purposely removed from the deposited fabrics. A contact angle goniometer (Dropletter A-100, Maist) was employed to obtain the water contact angles (WCAs) at ambient temperature. For each sample, at least 3 positions were measured and the average WCA was recorded. X-ray diffraction (XRD) of the CNT fabrics was performed on a Rigaku MiniFlex 600 X-ray diffractometer with a Cu Kα X-ray source. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409PC thermal analyzer in the atmosphere of air at a heating rate of 10 °C/min from 25 to 800 °C. A spectroscopic ellipsometer (Compe EASEM-2000U, J.A. Woollam) with an incident angle of 70° was used to determine the thicknesses of the ZnO films deposited on Si wafers.

2.4. Permeability and separation tests

The pure water permeability (PWP) and BSA retention tests were performed under 1 bar in a stirred filtration cell (Amicon 8010, Millipore). For the retention tests, BSA was dissolved in the PBS buffer solution at a concentration of 0.5 g/L. BSA retentions were tested by
measuring the concentrations of the BSA both in the feed and permeate solutions using a UV–vis spectrometer (NanoDROPR 2000C, Thermo Scientific) at the wavelength of 280 nm. To induce the BSA solution to permeate through the highly hydrophobic pristine CNT membrane, the membrane was first wet with ethanol and then subjected to BSA filtration. The PWPs and BSA retentions were calculated by Eqs. (1) and (2), respectively:

$$\text{PWP} = \frac{V}{A \times t \times \Delta P}$$  \hspace{1cm} (1)

where $V$ (L) is the volume of the pure water penetrating through the membrane, $A$ ($m^2$) is the effective membrane area, $t$ (h) is the operation time, and $\Delta P$ (bar) is the operation pressure.

$$R = \frac{C_f - C_p}{C_f}$$  \hspace{1cm} (2)

where $C_f$ and $C_p$ are the BSA concentrations (g/L) in the feed and the penetrative solutions, respectively.

Dextran with different molecular weights (10, 40, 70, and 500 kDa, Sigma-Aldrich) were dissolved in deionized water and their concentrations were 2.5 g/L, 1.0 g/L, 1.0 g/L, and 2.0 g/L, respectively.

The filtration of dextran solutions was analyzed by gel permeation chromatography (Waters 1515). The retention of dextran was determined by measuring the dextran concentrations of feed and permeate solutions, respectively.

The molecular weight cut-off (MWCO) of the membrane was defined as the molecular weight of the dextran corresponding to a 90% rejection level.

3. Results and discussions

3.1. Morphologies of ZnO-deposited CNT fabrics

In addition to deposit on CNT fabrics, we also deposited ZnO on Si wafers to investigate the growth rate of ZnO under the deposition conditions. The ZnO film was linearly increased in thickness with rising ALD cycle numbers. The average growth rate per cycle (GPC) is determined to be $\sim 0.18$ nm, which is similar to GPCs reported by others [44]. As shown in the SEM images in Fig. 1a, the pristine CNT fabric exhibits a fibrous morphology with irregular pores generated by the neighboring CNTs, and the tubes have a smooth surface before deposition. As shown in Fig. 1b-f, the surface coverage of the ZnO nanoparticulates on the CNTs was increased with rising ALD cycles. Fig. 1b shows the surface morphology of the membrane subjected to 20 ALD cycles. Numerous fine particles with sizes of 5-15 nm are observed on the surface of individual CNTs. It is believed that ZnO particles were preferentially nucleated on defects or impurities present on the outer surface of CNTs. It has been reported that in ALD on hydrophobic carbon materials including graphene and CNTs the inert surface lacks active sites even for very reactive precursors. Nevertheless, adsorption can still occur on surface defects [33]. The number and size of ZnO nanoparticulates were increased with 40 ALD cycles (Fig. 1c). There is a very high coverage of ZnO nanoparticulates on the tubes with 60 ALD cycles (Fig. 1d). With even higher ALD cycles, neighboring ZnO nanoparticulates were progressively approaching each other as a result of the enlarged sizes, thus forming a nearly full coating along the CNTs (Figs. 1e and 1f). To further investigate the flexibility of the ALD-modified CNT fabrics, we folded the pristine and 60-cycle-deposited CNT fabrics for dozens of times, and both of them survived from the folding test, which illustrated that the ALD-modified CNT fabric maintained the good flexibility as the pristine fabrics (Fig. S1).

The deposition of ZnO as isolated particulates on the surface of CNTs in the initial stage of ALD is caused by the chemically inert nature of CNTs. On such inert surfaces barely having any active sites, the precursors are absorbed on defects/impurities on the surface and then nucleation occurring. Subsequent ALD cycles result in the outgrowth of ZnO particulates from the previously formed nuclei. This mode of ZnO growth on CNTs is confirmed by the mass gain of the CNT fabrics with different ALD cycles. Mass gain per cycle (MGPC) is defined as the weight gain of ALD-deposited CNT fabrics per cycle compared to the pristine CNT fabrics. As can be seen from Fig. 2, the MGPCs of ZnO-deposited CNT fabrics with 20, 40, 60, 80, and 100 ALD cycles was 1.31%, 4.92%, 5.91%, 6.07%, and 5.96%, respectively. The low MGPC in the initial 20 cycles could be ascribed to the slow nucleation stage on the defective sites on the nanotube wall. After 40 ALD cycles, the MGPC of the CNT fabric was greatly increased to 4.92%, and with the further increment of ALD cycles, the MGPC was apparently enhanced. The CNT fabrics subjected to different ALD cycles obtained higher mass gain compared with our previous work about ALD of metal oxides on porous polymer membranes [45], and there are two reasons for the remarkable mass gain of the deposited CNT fabrics. Firstly, the density of the CNTs is 1.3-1.4 g/cm³, while the density of the ZnO is 4 times heavier (5.6 g/cm³) than the CNTs; Secondly, combining with the excellent step coverage achieved by ALD, the highly porous CNT fabrics were almost totally wrapped by ZnO (Fig. 1), so the mass of the CNT fabrics increased sharply after deposition. With the progressive enlarging and approaching of ZnO nanoparticulates, the deposited fabric exhibited a reduced specific surface area for ZnO growth. Consequently, the MGPC was decelerated after completion of the nucleation with the further increment of ALD cycles.

3.2. Crystalline structure of ZnO-deposited CNT fabrics

We used XRD to study the crystalline structure of the ZnO-deposited CNT fabrics. As presented in Fig. 3, the peaks at 24.9° and 43.3° are originated from (002) and (100) plane of CNTs (JCPDS 58-1638). The peaks at 28 of 31.5°, 34.6°, 36.1°, 47.2°, 57.1°, 62.8°, and 67.9° correspond to (100), (002), (101), (102), (110), (103), and (112) crystal planes of the hexagonal wurtzite ZnO (JCPDS 36-1451), respectively. For the fabric with 20 ALD cycles, the ZnO diffraction peaks are weak due to the nucleation at the initial stage and the very limited amount of the deposited ZnO. This confirms our previous discussions with SEM results. The broadened XRD peaks imply the existence of nanocrystallites. The diffraction peaks become increasingly strong with higher ALD cycles. Especially, the three peaks of (100), (002) and (101) are significantly strong at the CNT fabric with 80 and 100 cycles, indicating the progressively increased amount of ZnO deposited on the CNT fabric. We further examined the microstructure of the ZnO-deposited tubes by TEM. As shown in Fig. 4a, there is an evident morphology of clusters of nanoparticulates adhering along with the surface of the CNT. High-resolution TEM was further carried out to investigate the crystalline structures of ZnO nanoparticulates. As can be seen from Fig. 4b, the typical spacing of lattice fringe is determined to be 0.28 nm, corresponding to the (002) crystal plane of hexagonal wurtzite structure of ZnO. Therefore, from XRD and TEM characterizations, we understand that ZnO has been grown on the surface of CNTs as nanocrystals and this is consistent with previous works reporting that ZnO is easy to crystallize in the ALD process [46].

3.3. Surface wettability of ZnO-deposited CNT fabrics

The wettability of CNT membranes plays a significant role in determining their permeation [47]. Herein, WCA of the pristine and ZnO-deposited CNT fabrics were measured. With the deposition of ZnO, the CNT fabrics are expected to have enhanced affinity towards water. As illustrated in Fig. 5, the WCA were continuously decreased as the number of ALD cycles increased. The WCA of the pristine CNT fabric is $\sim 115°$, indicating a strong hydrophobic nature. The WCA was significantly decreased to $\sim 58°$ after 20 cycles. This is because ZnO has much higher surface energy than CNTs, therefore, the ZnO-deposited CNT fabric showed enhanced hydrophilicity in spite of the relatively small amount of ZnO being deposited. An evident decrease of the WCA to as low as $\sim 35°$ was observed for the CNT fabric with 40 ALD cycles.
As we discussed in Section 3.1, CNTs were further covered due to the intergrowth of ZnO nanoparticulates and the hydrophilicity of the CNT fabric was further enhanced. With further improved coverage of ZnO on CNTs the WCA was reduced to ~21° after 80 ALD cycles, implying a strong hydrophilic surface of the deposited CNT fabrics. Such a wettability transition from strong hydrophobicity to high hydrophilicity for the CNT fabrics by ALD of ZnO is very much desired for their applications as separation membranes in aqueous environments.

3.4. Stabilities of ZnO-deposited CNT fabrics

To further demonstrate the deposition of ZnO on CNT fabrics, we performed TGA on them before and after ZnO deposition. As can be seen in Fig. 1, the mass gain per cycle increases with the number of ALD cycles. This indicates that the deposition process is stable and consistent across different cycles.

Fig. 1. SEM images of (a) the pristine and ZnO-deposited CNT fabrics with (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 ALD cycles, respectively.

Fig. 2. Mass gain per cycle of ZnO-deposited CNT fabrics as a function of ALD cycle numbers.

Fig. 3. XRD patterns of ZnO-deposited CNT fabrics with various ALD cycles. The characteristic diffraction peaks of CNTs are marked with asterisks.
seen from Fig. 6, after calcination in air at 800 °C the pristine CNT fabric exhibited a residual mass of 9.5% which can be ascribed to the residual catalysts and/or inorganic impurities generated from the production of CNTs by the chemical vapor deposition process. The net residual masses after burning the CNT fabrics with 20, 40, 60, 80, and 100 ALD cycles were 21.0%, 48.8%, 69.9%, 73.8%, and 76.8% (the residual mass of the pristine CNT fabric has been subtracted), respectively. It is clear that the deposited ZnO was accounted for a relatively higher weight percentage in the deposited CNT fabrics. This is because that ZnO (5.6 g/cm³) has a much larger density than CNTs (1.3–1.4 g/cm³). The residual mass difference between the pristine and deposited CNT fabrics with different ALD cycles confirms that ZnO has been successfully deposited on the CNT membrane, and implies that the deposition amount of ZnO on the CNT membrane is increased with the increase of ALD cycles.

To investigate the structural stability of the CNT fabrics after ZnO deposition, we immersed the pristine and 100-cycle-deposited CNT fabrics in ethanol and challenged them with ultrasonic treatment at the power of 150 W for 20 min. We then compared the appearance and morphology of the CNT fabrics before and after ultrasonic treatment. It can be seen from Fig. 7a–b that the pristine CNT fabric became fluffy after ultrasonication, suggesting loose entanglement between individual CNTs. Moreover, they can be easily disassembled by gentle contact with tweezers. In contrast, for the CNT fabrics subjected to 100 ALD cycles, no cracks or apparent change could be observed after identical ultrasonication treatment (Fig. 7c–d). Moreover, we did not observe any noticeable morphology change under SEM and the original structure was maintained for the CNT fabric subjected to 100 ALD cycles before and after ultrasonication, indicating the greatly enhanced adhesion between individual CNTs after ZnO deposition. The enhanced structural integrity and stability of the ZnO-deposited CNT fabrics should be attributed to the "gluing effect" of the deposited ZnO to the interleaved CNTs. In the presence of numerous fibrous CNTs entangled as a 3D porous configuration, ALD takes place throughout the entire thickness of the CNT fabrics, forming a correspondingly 3D interconnected ZnO layer wrapping CNTs. The deposited ZnO works as "glue" to make the originally loosely contacted CNTs tightly adhere with each other, thus forming a stabilized composite structure. To further investigate the attaching strength between the ZnO layer and the fabrics, we also challenged the 60-cycle-deposited CNT fabric with ultrasonic treatment. There are no noticeable morphology changes after ultrasonic treatment, which exhibiting the excellent adhesion between the ZnO layer and the fabrics (Fig. S2).

3.5. Ultrafiltration Performances of ZnO-deposited CNT fabrics

ZnO-deposited CNT fabrics are highly porous with 3D interconnected nanoporosities and highly hydrophilic, allowing water to permeate while reject big species. Therefore, they are expected to work as selective membranes suitable for water treatment. We finally investigated the water permeabilities and rejection to BSA of the ZnO-deposited CNT fabrics with different ALD cycles to evaluate their separation performances and the results are given in Fig. 8a. The pristine CNT fabric is strongly hydrophobic, and water cannot wet it. As a result, the PWP of pristine CNT fabrics is zero even under a transmembrane pressure up to 4 bar. In contrast, the ZnO-deposited CNT fabrics exhibit appreciable water permeabilities. As can be seen from Fig. 8a, the PWP was first increased and then decreased with the increasing ALD cycles. The CNT fabric exhibit a permeability of 253 L m⁻² h⁻¹ bar⁻¹ after ZnO deposited for merely 20 cycles. Water permeability was further increased to 430 L m⁻² h⁻¹ bar⁻¹ with 40 cycles. However, with further increasing ALD cycles, water permeability significantly dropped. For example, the PWPs of 60 and 80 ALD cycles were 177 and
84 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), respectively. Such a change in permeability should be attributed to the competing effect of enhanced surface hydrophilicity and reduced pore sizes. Surface hydrophilicity and pore sizes are the two main factors influencing the water permeabilities of membranes. For membranes with higher ALD cycles, the reduced pores are playing an overwhelming role compared to the enhanced hydrophilicity, resulting in decreasing PWP. Moderate ALD cycles (40 cycles) only led to slight shrinkage in pore sizes, however, the hydrophilicity was significantly enhanced, which is confirmed by the reduction of WCA from 115° to 35°. Therefore, the significant improvement of hydrophilicity could evidently improve PWP while the pore reduction by ZnO deposition can be neglected, leading to greatly increased PWP. With further increasing ALD cycles (> 40 cycles), the improvement in hydrophilicity of the membrane is much less pronounced, and the effect of pore size reduction became the dominant one. Therefore, the PWP started to decrease from this peak value.

We also investigated the rejection properties of the pristine and ZnO-deposited CNT fabrics. As shown in Fig. 8a, the pristine membrane exhibited a minor rejection of 10.3%. After deposition of ZnO for 40 cycles, the rejection was remarkably increased to 58.1%, indicating the strong efficiency of ALD in upgrading of the size-discriminating performances. Further increment in ALD cycles led to relatively slow increase in rejection. The retention rate was insignificantly increased from 78.7% with 60 ALD cycles to 89.8% with 80 ALD cycles. We note that both the permeability and selectivity of the CNT fabrics were greatly enhanced after ZnO deposition with a small number of cycles. Such a simultaneous improvement both in the permeability and rejection is originated from the homogeneous deposition of the ultrathin layer of hydrophilic ZnO on the CNT fabrics. In addition, the ALD-modified fabrics showed excellent stability along with the time course before and after the retention test, and there is only 10% PWP decrement after retention test (Fig. S3). The deposited ZnO influenced the permeability and filtration performance of the membrane from two different aspects: enhancing the hydrophilicity and reducing the pore sizes. Enhancing hydrophilicity played the dominating role when ALD cycles was less than 40 and reduction in the pore size played a major role with more cycles in determining the PWP as we discussed above. However, as the size-discriminating property of UF membranes is exclusively determined by the effective pore size, the retention to BSA was increased along with rising ALD cycles. As a result, the water permeability was first increased and then decreased whereas the retention showed an increasing trend. We note that the simultaneous increase in water permeability and rejection for the CNT fabrics subjected to moderate ZnO deposition is consistent with our previous works [35,37], confirming that ALD of metal oxide is a general route to break the trade-off effect of hydrophobic membranes. To further investigate the separation performance of the deposited CNT fabrics, we tested the MWCO of the 60-cycle-deposited CNT fabric. As shown in Fig. 8b, the 60-cycle-deposited CNT fabrics recorded a MWCO of 64 kDa, illuminated that the fabric can reject 90% of molecules with a molecular weight of 64 kDa, which means that the retention of BSA (with a molecular weight of 67 kDa) should be higher than 90%. However, as indicated in Fig. 8a, the retention of 60-cycle-deposited CNT fabrics towards BSA was 78.7%, smaller than the value deduced from the MWCO. There were two possible reasons responsible for the smaller retention of the BSA than the MWCOs. Firstly, the test condition of the BSA rejections and MWCOs are different. The BSA concentration was 0.5 g/L, while the total dextran was 6.5 g/L. The large concentration difference may influence these two molecules passing through the fabrics. Secondly, the different shape of BSA (ellipsoid) and dextran (linear thread-like) may also affect the separation process [48].

According to the permeability and rejection of the ZnO-deposited CNT fabrics we conclude that they efficiently work as UF membranes. Their permeability and rejection can be flexibly tuned in a relatively wide range, and are comparable to many UF membranes prepared by the typical phase inversion process. Moreover, the permeaselectivity of our CNT-based membranes is expected to be further improved by deliberately controlling the ALD process to have an asymmetric structure [49]. Even further, ZnO was used in the current study as the model metal oxide to demonstrate the capability of ALD in the production of water-permeable ultrafiltration membranes using CNT fabrics as the substrates. However, because of the versatility of ALD, it is
prepare membranes with additional functionalities including catalysis, straightforward to expect that a number of other materials, for example, dextrans with di-

Fig. 8. (a) Pure water permeability and BSA retention of the CNT fabrics subjected to

straightforward to expect that a number of other materials, for example, metal oxides, metals, can be ALD-deposited on the CNT fabrics to prepare membranes with additional functionalities including catalysis, photocatalysis, antimicrobial, etc. Moreover, considering the excellent mechanical, thermal, and chemical stabilities of CNTs thus-produced membranes may find important applications in harsh environments, for example, high temperature, erosion, where common membranes cannot tolerate.

4. Conclusions

membranes. Considering the excellent mechanical, thermal, and chemical properties of the ALD-modified CNT fabrics, they are expected to find important applications in harsh conditions where common membranes cannot survive.

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Appendix A. Supplementary material

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References


