Highly permeable and robust membranes assembled from block-co-polymer-functionalized carbon nanotubes

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ABSTRACT

The fabrication of homogenous integrated layers of assembled carbon nanotubes (CNTs) on porous substrates for advanced membranes via vacuum filtration remains a significant challenge due to the aggregation of CNTs. Here we report the composite membranes with both high flux and good mechanical robustness produced from functionalized CNTs through direct coating with amphiphilic block copolymer. Chemically crosslinked CNT layers are tightly adhered to the substrate, rendering a strong mechanical stability to the composite membranes. The thickness of the separation layer as well as the permeability of the membranes can be readily tuned simply by changing the deposition amount of CNTs. The membranes with a moderate nanofiber coverage are capable of complete removal of 10-nm-particles while offer a remarkable pure water flux higher than $5.7 \times 10^3$ L/(m$^2$ h bar), suggesting their high efficiency in the purification of liquids contaminated by tiny colloids or particulates.

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1. Introduction

As one efficient and environmentally friendly strategy, membrane technology manages to provide a variety of solutions in all walks of life including seawater desalination, wastewater reuse and groundwater treatment [1–3]. Among the pressure-driven membranes in aqueous applications, namely micro-, ultra-, nanofiltration and reverse osmosis membranes, ultrafiltration (UF) membranes which are able to reject nanometer-sized particulates and colloids under relatively lower driving forces have been widely applied in industry and tremendous efforts are continuously made to further increase the permeance of UF membranes at negligible expense of selectivity [4]. For UF membranes which are based on size-sieving mechanism, there are some crucial factors that determine the separation performances, including the surface morphology, pore size and the size distribution, etc. [5]. The trade-off effect between selectivity and permeability of most membranes urgently needs to be broken by altering these factors, e.g. increasing the porosity and conducting surface modification [4].

Compositing UF membranes of large porosity and narrow pore size distribution as selective layers onto a macroporous supporting substrate can be considered as a promising strategy for the fabrication of energy-efficient membranes. As one alternative origin for the selective layers, one-dimensional nanofibers (including also nanowires and nanotubes) with high aspect ratios lead to large specific surface area, high porosity of the nanofiber membranes, and more importantly, the consequent superiority in permeation. Moreover, with such advantages as three-dimensional continuous porous structures and small effective pore sizes, the high permeability and simultaneously high retention of the nanofiber membranes might be well guaranteed. A number of polymeric nanofibers membranes have been applied in some areas. Though promising, the low mechanical strength greatly obstructs their further applications. With the mechanical strength of tensile modulus as high as 1–2 TPa and tensile strength of 200 GPa, carbon nanotubes (CNTs) can meet the mechanical strength demand of the membranes under relatively harsh conditions [6]. Commercial feasibility of the preparation for CNTs-based separation membranes has been realized thanks to the scale-up and manufacture which reduces the cost of CNTs [7].

Vacuum filtration has been greatly applied in the past decades to fabricate composite membranes with nanofibers as the building blocks for the selective layers due to its simplicity [8–10]. However, two major factors need to be considered for such synthetic route, namely the good dispersibility in solutions of the nanofibers before filtration and the strong adhesion between the nanofibers after filtration. As for CNTs with strong intertube interactions present locally along the tubes, they have the tendency to interweave, and therefore form an inhomogeneous and unstable dispersion. Purification of CNTs and addition of surfactant and polymers will lead to highly dispersed CNTs; and uniform CNTs

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membranes can be generated upon vacuum filtration [11,12]. A number of works have been reported for the preparation of membranes or filters composed of randomly stacked CNTs [13–15]. In most cases, CNTs without any pretreatment were directly filtrated on the porous substrates and usually large amount of CNTs were used to generate CNTs layers thick enough to maintain heavily entangled, integrated layers. It was found that these thick CNT layers can be easily peeled off from the substrate and they were typically used as free-standing, symmetric membranes [13,14]. Such thick and symmetric structures would significantly compromise permeance. Recently, thin layers of single-walled CNTs (SWCNTs) have been filtrated on porous substrates to form composite membranes exhibiting very high permeance [16]. Unfortunately, SWCNTs require very tedious and low-efficient dispersion treatment and their cost is extremely high. Therefore, it is highly appealing to assemble cheap multiwalled CNTs on macroporous substrates to form thin but robust selective layers, allowing highly permeable and selective filtrations.

In our previous work, homogeneous dispersion of multiwalled CNTs with excellent stability has been successfully produced upon the addition of amphiphilic block copolymers, polystyrene-block-poly(4-pyridine) (PS-b-P4VP, shortly S4VP), into the dispersion of CNTs in acetic acid [17]. Here in this work, for the first time we demonstrated the fabrication of block-copolymer-functionalized CNTs composite membranes. This simple yet effective method involves vacuum filtrating the selective layers, well dispersed CNTs with active P4VP chains onto the macroporous polyethersulfone (PES) substrate membranes. The composite membranes exhibited highly controllable permeance via changing the mass of S4VP/CNTs nanofibers. Moreover, the mechanical properties of CNTs and the chemical crosslinking of the P4VP chains stabilize the CNTs layers, which provide the composite membranes greater potential in industrial applications. Compared to other membranes using nanofibers as the building blocks, our membranes are distinguished for their easy and affordable availability of the building materials (CNTs) and the mechanical robustness. Specifically, such membranes are expected to find interesting applications in the separation of nanosized colloids, particulates, and proteins with similar sizes.

2. Experimental

2.1. Materials

Block copolymer S4VP ($M_n(PS)=12,000$ g/mol, $M_n(P4VP)=1700$ g/mol, $M_w/M_n=1.09$), polyethylene glycol (PEG, $M_n=203000$ g/mol, $M_w/M_n=1.14$) were purchased from Polymer Source Inc., Dorval, Canada and used without further treatment. CNTs (inside diameter: 4.5 ± 0.5 nm, outside diameter: 10 ± 1 nm, length: 3–6 μm) with purity higher than 98% and 1,4-diodobutane (DIB) with purity higher than 99% were purchased from Sigma-Aldrich. PES membranes with an average pore diameter of 450 nm (Tianjin Jinteng Instrument Co. Ltd.) were used as substrates. Acetic acid and ethanol with purity ≥ 99.5% were obtained from local suppliers. Monodisperse gold colloidal nanoparticles with a diameter of 10 nm were purchased from British Biocell International.

2.2. Preparation of S4VP/CNTs composite membranes by vacuum filtration

The general strategy for fabricating composite membranes is shown in Scheme 1. The preparation of the S4VP-coated CNTs was described detailed in our previous work [17]. Briefly, a suspension of CNTs in acetic acid (5 mg in 10 g) was prepared and sonicated for 30 min with a power of 350 W. Then 10 mg of S4VP was added and sonicated for another 2 h with the power of 100 W. For the preparation of composite membranes, the as-synthesized 0.15 wt% S4VP-coated CNTs solution was cooled down to room temperature and diluted for 50 times with ethanol as the stock solution. The dispersion formed a depositing layer on the surface of the substrate membrane by vacuum filtration. In a typical experiment, one piece of PES substrate membrane was immersed in ethanol for 10 min and then fixed in a glass vacuum filter (Model 16306, Sartorius AG) connected to a suction filtration flask. 3 g of ethanol

Scheme 1. The preparation process of the composite membranes: dispersion of CNTs with the assistance of sonication (a); the addition of S4VP block copolymers into highly dispersed CNTs (b) to generate stable S4VP/CNTs dispersions (c); the vacuum filtration of S4VP/CNTs dispersions onto the macroporous substrates (d) and the chemical crosslinking of the composite membranes (e).
was added for filtration to thoroughly prewet the PES membrane. Various amounts of S4VP/CNTs dispersions ranging from 5 to 20 g were filtered through the PE S substrate membranes under a reduced pressure of 3 kPa. 6 mL of ethanol was subsequently filtered through the membrane for 3 times to wash away the residual acetic acid in the composite membrane. The composite membranes were air dried for 30 min at the temperature of 60 °C and then crosslinked in the vapor of DIB at 80 °C for 2 h under vacuum [18,19]. After crosslinking, the composite membranes were cooled down to room temperature and immersed in ethanol for 30 min and then thoroughly washed with fresh ethanol to remove the residual DIB. The membranes were finally dried in air at room temperature and were ready for usages.

2.3. Characterizations

The surface morphology of composite membranes was observed on a Hitachi S4800 field emission scanning electron microscope (FESEM) operated at 5 kV. A thin layer of Pt/Pd alloy was sputter coated on the samples to avoid surface charging during SEM observations. The detailed morphology of the S4VP-coated CNTs was examined on a JEM-2100 transmission electron microscope (TEM) operated at 200 kV. Water contact angles of different composite membranes were obtained from a contact angle goniometer (DropMeterA-100P, MAIST). Fourier transform infrared spectroscopy (FTIR) was recorded on a Thermo Nicolet 8700FT-IR spectrometer in the transmission-mode (32 scans, 4 cm−1). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250 XPS system using a monochromatic Al Kα line X-ray source. The as-prepared S4VP/CNTs stock solution was pre-filtered by a PVDF membrane with a nominal pore diameter of 0.22 μm to eliminate the S4VP micelles possibly coexisting with the coated CNTs, and then deposited on silicon substrates for XPS characterizations after drying. Scratch tests were carried out on a nanoindentation instrument (Nano-Test Vantage, Micromaterials) to analyze the interfacial adhesion of between the PES substrate support and the S4VP-coated CNTs layer in the composite membranes. Indentation tests were also performed on this instrument to measure the mechanical properties of the composite membranes with the S4VP/CNTs layer and with the pure polymer layer assembled from S4VP micellar nanofibers, respectively. The latter membrane was prepared following our previous method [9].

2.4. Filtration experiments of composite membranes

The water flux and the retention to PEG and gold nanoparticles of the composite membranes were determined using a stirred filtration cell (Amicon 8003, Millipore Co., Billerica, MA) under the pressure of 0.02 MPa. Typically, the composite membrane with a diameter of 25 mm was placed in the filtration cell with the S4VP/CNTs layer side of the membrane as the permeating side. For the PEG retention test, 5 mL of PEG solution at the concentration of 0.5 g/L was filtered. After filtration for 1–2 min, about one half of the liquid was left in the cell and we terminated the filtration. The concentration of filtration solution as well as feed solution was characterized by Gel Permeation Chromatography (Water 515). The concentration of gold nanoparticles in the feed, permeate and concentrated solutions were obtained by a UV–vis spectrophotometer (NanoDROPO 2000C) at the wavelength of 530 nm.

3. Results and discussions

3.1. Morphologies of S4VP-coated CNTs nanofibers

We first tried to directly filter the as-received, pristine CNTs onto macroporous substrate membranes to produce a selective layer. However, the efforts failed as the pristine CNTs cannot form a stable suspension in any solvent we investigated, imposing difficulties in performing the filtration process. Even for the portion of CNTs deposited on the substrate membranes did not establish a homogeneous layer throughout the substrate surface and they were easily detached from the substrate. Such challenges as low dispersibility and insufficiently adhesion between nanotubes can be attributed to the inert surface and large length-diameter ratio of CNTs [20]. Therefore, it is a prerequisite to render CNTs a good dispersibility before we can use CNTs as building blocks for the selective layer of membranes. We previously demonstrated that the amphiphilic block copolymer S4VP, were effective in coating CNTs with the assistance of ultrasonication, and the coated CNTs exhibited excellent dispersibility in polar solvents. In this work, S4VP-coated CNTs were used as active building blocks to build selective layers on macroporous substrates to prepare highly permeable composite membranes. With the fibrous-like morphology and narrow-distributed diameter of ~20 nm, the sonication-assisted S4VP/CNTs solutions display the advantages such as uniform dispersion and high stability, which serve as excellent building blocks for the generation of composite membranes with high performances. On one hand, the mechanical strength of the composite membranes would be improved as the interior of the composite fibers are filled with CNTs. On the other hand, with exterior layer composing of pyridine-enriched P4VP block copolymers, chemical crosslinking will take place to enhance the interactions between fibers and eventually improve the stability of the composite membranes.

As shown in Fig. 1(a), we easily discerned from the TEM images the core/shell structures of the coated CNTs: a darker core sheathed with a uniform light shell. Fig. 1(b) is the high resolution TEM of the composite nanofiber, from which we can clearly allocate the dark core with crystalline lattices as the CNTs and the
light shell is the polymer. Such a core/shell structure clearly indicates that CNTs are coated by the copolymer. Furthermore, from Fig. 1(b) we can determine that the integrated diameter of the coated CNTs is approximately $\sim 20$ nm and the thickness of the copolymer layer is $\sim 5$ nm. The coated CNTs form a stable solution in polar solvents, e.g. acetic acid, ethanol and their mixtures. The illustration picture in inset of Fig. 1(a) was the solution of coated CNTs prepared in acetic acid followed by dilution with ethanol at the ratio of 1:50. The solution maintains its clear and semi-transparent appearance for months at ambient environment, suggesting that the addition of S4VP greatly improves the dispersion of CNTs in polar solvents because of the presence of active P4VP blocks on the outermost surface of the coated CNTs.

3.2. Surface properties of S4VP/CNTs composite membranes

We then applied the vacuum filtration technique to deposit the coated CNTs on the macroporous PES substrates. As CNTs used in this work have a length of 3–6 μm which is one order of magnitude larger than the pore diameter of the substrate membrane, the CNTs originally dispersed in the solution are completely collected on the surface of the substrate membrane by forming a “filtration cake”. The complete retention of CNTs by the PES membrane is also evidenced by the colorless appearance of the filtrate which is in stark contrast to the dark color of the feeding solution containing CNTs. The as-prepared CNTs layer does not have a strong adhesion to the PES substrate and the CNTs are easily detached from the substrate and dispersed again in water and other polar solvents. The S4VP-coated CNTs layer must be fixed on the substrate before it can be used in separation. To this end, we exposed the as-prepared CNTs/PES composite structures to the vapor of DIB to crosslink the P4VP blocks which existed on the outermost layer of the S4VP-coated CNTs. The crosslinking reaction is based on the quaternization of pyridyl groups on the P4VP blocks of S4VP by the bifunctional alkyl halide, DIB. When the two ends of a DIB molecule react with pyridyl groups anchored to different tubes, the crosslinking occurs, connecting two different but adjacent CNTs. The CNTs are densely packed, allowing the P4VP chains from different tubes to be frequently contacted. Therefore, the crosslinking taking place between different tubes should be accounted for a considerable portion in all types of quaternization involved in this system. As a result, the CNTs are tightly bound with each other and fixed as an integrated layer to the PES substrate after crosslinking.

We first used FT-IR to characterize the composite membranes before and after chemical crosslinking. A characteristic peak of P4VP after quaternization reaction is expected to appear at the wavenumber of 1645 cm$^{-1}$; however, this peak is overlapped by the characteristic peak of pristine CNTs (spectra not shown). Alternatively, we utilized XPS with higher sensitivity to analyze the surface composition of the membranes before and after crosslinking. Fig. 2(a–c) displays the survey, the corresponding high-resolution N 1s and I 3d spectra of the pristine and crosslinked CNTs layers, respectively. As shown in Fig. 2(a), the survey of the pristine CNTs shows three main emission peaks: 284.6 eV for C 1s, 399.0 eV for N 1s, and 532.1 eV for O 1s. The presence of a small peak corresponding to O 1s was due to the surface absorption of H$_2$O and CO$_2$, which is very common in XPS analysis [21,22]. Since N element is only originated from the pyridyl groups of S4VP, the XPS results confirmed again the successful coating of S4VP onto CNTs.

After the CNTs were crosslinked via the quaternization reaction, the emission peaks of C 1s and O 1s remained prominent whereas that of N 1s is weakened. The peak intensity of O 1s is enhanced compared with the pristine one before crosslinking, which might be ascribed to the stronger adsorption of water of the quaternized P4VP. After quaternization, the pyridyl groups in P4VP blocks are converted into quaternary ammonium salt, which has a stronger hydrophilicity than the pristine P4VP block and adsorbs more
water vapor from ambience which is difficult to be completely removed in the XPS tests. Interestingly, the peak intensity of N 1s decreases after crosslinking as it splits into two peaks, which could be evidently discerned in the high resolution spectrum shown in Fig. 2b. In contrast to a single stronger peak of the N 1s spectrum of the CNTs before crosslinking, the N 1s peak recorded from the quaternized sample showed two separated peaks, located at 399.0 eV and 402.1 eV, respectively. The peak position of 399.0 eV N 1s was the same as the pristine sample, which corresponds to the uncharged pyridyl rings of the P4VP chains. The other peak emerging at 402.1 eV was typically found for cationized nitrogen atoms of ammonium groups [23,24], which confirms the successful quaternization reaction. Moreover, the two separated peaks of nitrogen also indicate that the quaternization reaction does not completely convert all pyridyl groups into pyridinium cations. The peak area ratio can be calculated as \([N^+]/([N^+]+[N])=0.34\), suggesting that the degree of the quaternization reaction was approximately 34%. In addition, as shown in Fig. 2c the emission peaks from iodine located at the binding energy of 618.4 eV and 629.7 eV can also be detected from the high-resolution XPS spectrum of the crosslinked sample, representing I 3d_{5/2} and I 3d_{3/2}, respectively [25,26]. This indicates the incorporation of DIB molecules which are the only source of iodine into the sample and further confirms the occurrence of the quaternization reactions.

3.3. Morphologies of S4VP/CNTs composite membranes

Fig. 3 exhibits the morphologies of the S4VP/CNTs nanofibers deposited on the substrate membranes after filtration with various amounts of fibers dispersed in ethanol. At relatively low amount of filtrated nanofibers, for instance, 36.6 μg/cm², the massive network of nanofibers maintained the complete coverage of the

![Fig. 3. Surface (a, b) and cross-sectional (c, d) SEM images of the composite membrane with a nanofibers deposition amount of 36.6 μg/cm². Cross-sectional (e–g) SEM images of composite membranes with different deposition amounts of nanofibers: (e) 73.2, (f) 109.8 and (g) 146.4 μg/cm².](image-url)
substrate membrane with a uniform and smooth surface. As can be seen from Fig. 3(c, d), a composite structure consisting of nanofibrous selective layer and macroporous supporting layer can be clearly observed. The enlarged cross-sectional SEM image (Fig. 3(d)) of composite membranes displayed an interconnected selective layer with the thickness of 750 nm. Such a selective layer with the nanoporous structure can be attributed to the closely stacked and densely entangled nanofibers. The S4VP/CNTs nanofibers are tightly adhered and vertically compacted on the membrane surface without cracks or defects. The selective layers maintained the coverage of all the macropores when the amount of filtrated fibers increased to 146.4 μg/cm² (Fig. 3(g)). The apparently thicker selective layer with similar morphology indicated the selective layer thickness could be tuned by controlling the amount of stacked fibers on the surface of composite membranes. For instance, the thickness of selective layer increased to 1.6 μm when the deposition amount of nanofibers reached 73.2 μg/cm². The selective layer thickness continuously increased to 2.4 and 2.9 μm with further addition of deposited nanofibers, i.e., 109.8 and 146.4 μg/cm², respectively. These cross-sectional SEM images also clearly show the excellent uniformity in the thickness of the deposited S4VP/CNTs layers.

3.4. Mechanical properties of S4VP/CNTs composite membranes

For a composite membrane, there must be an interfacial adhesion strong enough between the selective layer and the underneath substrate to avoid the exfoliation of the top layer from the support [27]. Peeling will tend to occur when the interfacial stress surpasses a specific value, not to mention the exfoliation in the usage under harsh conditions. Considering the natural functionality of P4VP on the nanofiber surface, this part will concentrate on the interfacial adhesion between the nanofibers after crosslinking the surface P4VP and nano-scratch was applied. The critical load increased from 5.24 mN of the uncrosslinked membrane to 11.96 mN of the crosslinked one, implying that the interfacial adhesion doubled after the crosslinking (results were shown in Fig. 4(a)). Figs. 4(b and c) were the photographs showing the composite membrane before and after crosslinking challenged by ultrasonication under the power of 100 W for 10 min in the ultrasonic bath, respectively. They clearly showed that the fibrous layer was well preserved on the substrate for the crosslinked membrane after ultrasonication (as shown in Fig. 4(b)); however, the fibrous layer largely peeled from the substrate for the uncrosslinked membrane. The overall adhesion strength between the nanofibers, the fibrous layer and the substrate were improved through the simple crosslinking method. The high adhesion strength guaranteed the excellent permeation and separation performance of the composite membrane.

3.5. Permelectivity of the S4VP/CNTs composite membranes

Permeability and selectivity are important characteristics for the evaluation of membrane performances. Fig. 5 displays water flux and rejection of PEG versus deposition amount of S4VP/CNTs nanofibers. The pristine PES membrane exhibited a substantially large flux of 4.4 × 10⁴ L/(m² h bar) and a negligible rejection to PEG, which possessed a molecular weight of 20,300 g/mol. The water flux of the composite membrane with a deposition amount of 36.6 μg/cm² nanofibers decreased about 87% comparing to that of the original PES substrate membrane. At the meantime the PEG rejection rate of this composite membrane drastically increased to 52%. Such fluctuation in permeation and rejection was due to the significant decrement in effective pore size of the composite membranes upon the filtration of S4VP/CNTs micellar fibers and the establishment of the thin selective layers. Further increase of the S4VP/CNTs fibers deposition amount to 109 μg/cm² led to an even higher rejection of 87% and a flux of 2.7 × 10³ L/(m² h bar). The rejection rate to PEG remained at ~90% whilst water flux decreased despite of the continuous enhancement in the deposition amount of S4VP/CNTs fibers. The results indicated an excellent permeability of the composite membranes, which might be ascribed to the particular selective layers of S4VP/CNTs fibers with thin thicknesses and active surfaces, leading to reduced flow resistance [28]. Moreover, the S4VP/CNTs nanofibers with a uniform diameter of 20 nm and narrow size distribution were utilized in this work, which implies remarkably improved rejection ability of the composite membranes can be anticipated since the selective layers were bestowed a relatively smaller pore size.

Many factors, such as surface charging, surface roughness and surface hydrophilicity affect the permeability and selectivity of the membrane. As has been widely reported before, CNTs display a hydrophobic property due to its inert surface [29], which might...
cause poor permeability for the fabrication of separation membranes. To investigate the surface hydrophilicity of the membrane, contact angles were measured on the composite membranes before and crosslinking. As shown in Fig. 6(a), the contact angle of the composite membrane before crosslinking was ~141°. After crosslinking, the contact angle decreased to 104°. The reduction of the contact angle indicated that the surface hydrophilicity of the composite membrane considerably improved, which assigned to the synergetic effect of P4VP block on the surface of the S4VP-coated CNTs and the quaternization reaction. Such process may improve the surface hydrophobicity of the P4VP chains which has been verified in the XPS analysis. Coating of S4VP over CNTs along with quaternization moderately enhanced the hydrophilicity and we note that their hydrophilicity may further be improved using other post treatment, for example, coating of metal oxides by atomic layer deposition [30]. Therefore, a composite membrane with exceptional permeability compared to conventional CNTs composite membranes was effectively fabricated through the coating of S4VP following by crosslinking of the CNTs.

The modification of CNTs by coating S4VP empowered the superior permeability and selectivity performance of composite membrane. Furthermore, the rigid nature of CNTs endowed the composite membrane with an excellent mechanical strength [31]. We investigated the changes of flux as a function of filtration time to study its mechanical stability. As shown in Fig. 7, the flux of composite membrane with 109.8 µg/cm² deposited nanofibers showed a slight reduction in the first 30 min of filtration process, which should be attributed to the slight compaction of the nanofibers stacked on the substrate surface [32]. With the enduring of the filtration, the flux almost kept constant. Fig. 8 shows that there is a linear correlation between flux and the applied transmembrane pressures (TMPs) in the range of 0.2–2 bar for the composite membrane with 146.4 µg/cm² deposited nanofibers. Therefore, the composite membrane indicated a great mechanical stability of the composite membranes with the addition of CNTs. Furthermore, we compared the mechanical properties of the S4VP/CNTs layer prepared in this work and a pure polymer layer assembled from S4VP micellar nanofibers prepared in our previous work [9] by the nanoindentation method. We found that the rigidity of the S4VP/CNTs layer increased 3 times compared to the pure S4VP layer, while the elasticity modulus increased by 77%, indicating that the addition of CNTs could significantly improve the mechanical properties of the selective layers.

It has been demonstrated in the permeation tests that the size-selective separation performance of composite membranes was highly tunable simply by controlling the amount of deposited fibers. The separation efficiency was characterized by monodisperse gold nanoparticles with a diameter of 10 nm. Fig. 9 shows the absorption spectra variation of gold nanoparticle solutions. The characteristic absorption band of gold at 530 nm [9] diminished after permeation whilst intensified on the separation side of the composite membrane, indicating an entire rejection of the composite membrane with an nanofiber deposition amount of 36.6 µg/cm². Visual color changes of the gold nanoparticle solutions from pink representing the feed stock into colorless as for the permeate solution whereas the pink color darkened in the concentrate solution corresponding to the increased absorption...
intensity also confirmed the conclusion (Fig. 9 inset). Yu and coworkers prepared membranes from stacked carbonaceous fibers and obtained a pure water flow of $1.1 \times 10^4$ L/(m²h bar) and an effective rejection to gold particles with the diameter of 25 nm [33]. In comparison, here we successfully improved the water flux for more than 5 times and the prepared composite membranes were capable of completely rejecting even smaller nanoparticles with the diameter down to 10 nm. This concurrent improvement in permeability and rejection should be ascribed to the synergetic effect of the smaller diameter of the S4VP/CNTs fiber, the thinner thickness of the S4VP/CNTs fiber layer, as well as the enhanced water wettability of the selective layer.

4. Conclusions

In this work we report a robust methodology fabricating composite membranes with superior mechanical strength and separation performances simply by assembling S4VP/CNTs nanofibers onto a macroporous substrate. The adhesion of composite membranes was successfully improved via chemical crosslinking. Moreover, the addition of CNTs significantly enhanced the mechanical strength of the composite membranes. With a particularly uniform and well distributed diameter of 20 nm, the composite membranes were endowed with small effective pore sizes leading to tightened rejections. The permeability and selectivity of the composite membranes could be easily tuned by altering the deposition amount of S4VP/CNTs nanofibers. The composite membrane with the nanofiber deposition amount of $36.6 \mu g/cm^2$ is capable of completely reject gold nanoparticles as small as 10 nm while offers a remarkable pure water flux higher than $5.7 \times 10^4$ L/(m²h bar). Such advanced composite membranes with ultrathin selective nanofibrous layers are expected to find interesting applications where tiny particulates or colloidal substances are required to remove or concentrate with high efficiency and less energy input.

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References