Improvement of Polyamide Thin Film Nanocomposite Membrane Assisted by Tannic Acid–Fe$^{III}$ Functionalized Multiwall Carbon Nanotubes

Huiqing Wu,* Huazhen Sun,‡ Weijie Hong,† Long Mao,† and Yuejun Liu*†§

†School of Materials Science and Engineering, Xiamen University of Technology, 600 Ligong Road, Xiamen 361024, China
‡State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai 200433, China
§Key Laboratory of New Materials and Technology for Packaging, Hunan University of Technology, 88 Taishan Road, Zhuzhou 412007, China

ABSTRACT: Tannic acid–Fe$^{III}$ functionalized multiwall carbon nanotubes (TA-MWNTs) were successfully obtained through a simple and rapid procedure by forming a stable TA–Fe$^{III}$ complex coating on the MWNT surface. Hydrophilic TA-MWNTs can disperse well in the aqueous phase and help the formation of a polyamide (PA) thin film nanocomposite (TFN) membrane through interfacial polymerization. TA-MWNT concentration in the aqueous phase was adjusted to achieve the optimal water flux and salt rejection of the TFN membrane. The results reveal that, when 0.03% of TA-MWNTs are added, the optimized water flux of the TFN membrane reaches up to 31.4 L/m²h, 2.36 times of that of the neat PA membrane, along with a well-maintained Na$_2$SO$_4$ rejection. Furthermore, the as-prepared TFN membrane shows improved antifouling ability and good long-term stability. A significantly enhanced chlorine resistant capability of the TFN membrane is also presented, which can be ascribed to the radical capturing capability of phenol groups of TA as well as more oxidation-stable polyester bonds produced by the interaction between the phenol groups of TA and the acyl chloride groups of TMC. Assisted by TA-MWNTs, the TFN membrane is found to have prominent advantages over PA and MWNTs/PA TFN membranes.

KEYWORDS: Polyamide, tannic acid, nanocomposite, interfacial polymerization, carbon nanotubes

1. INTRODUCTION

Membrane-based separation technology has stimulated intense attention due to the urgent water shortage worldwide. As a type of press-driven membrane, a nanofiltration (NF) membrane generally possessing a molecular weight cutoff ranging from 200 to 1000 Da, has been extensively studied and widely applied in various areas such as the removal of heavy metal ions, water softening, and seawater desalination.¹ Currently, most NF membranes are thin film composite (TFC) membranes which are prepared by the interfacial polymerization between two immiscible aqueous and organic phases. Generally, the aqueous phase contains a nucleophile monomer (e.g., amines, alcohol), while an electrophile monomer (e.g., acid chlorides, isocyanates) dissolves in the organic phase, and a dense and selective top layer can be formed on the support membrane. Various reaction parameters, such as the kind of solvent and monomers, monomer concentrations, additive ingredient, reaction temperature, and time, have significant effects on the structure of the formed polymer layer and corresponding properties of NF membranes.² NF membranes with numerous kinds of polymeric surface layers have been explored until now, and among them, the polyamide (PA) membrane is used most often. Different water-soluble amines, such as piperazine (PIP), 1,3-phenylenediamine and its derivatives, and organic-soluble acyl chlorides like trimesoyl chloride (TMC) and isophthaloyl chloride, have been employed for the preparation of PA NF membranes.²,³ Nevertheless, neat PA membranes still suffer from some shortcomings such as insufficient water permeability, vulnerable membrane fouling, and poor chlorine resistance.⁴⁻⁸

The construction of thin film nanocomposite (TFN) membrane has proven to be a promising approach toward achieving improvement in membrane performance.⁹,¹⁰ Two major challenges should be addressed to obtain a high-performance TFN membrane.¹⁰⁻¹² First, nanomaterials usually tend to aggregate, leading to a nonuniform dispersion in the polymer matrix. The poor dispersity would bring about nonselective defects or large voids and thus the deterioration of membrane selectivity. Second, the compatibility between nanomaterials and the polymer matrix also has a remarkable

Received: July 5, 2017
Accepted: September 1, 2017
Published: September 1, 2017

DOI: 10.1021/acsami.7b09680
ACS Appl. Mater. Interfaces 2017, 9, 32255−32263
impact on the membrane properties and stability. Multiwalled carbon nanotubes (MWNTs) are a competitive candidate due to their outstanding mechanical, thermal, and electrical properties. The inner pore cavities of MWNTs also provide a favorable opportunity because water molecules could pass through nanotube pores with a speed that is orders of magnitude faster than those through other pores of similar size. However, the inert and super hydrophobicity of pristine MWNTs often cause serious problems of MWNTs dispersity and the compatibility between MWNTs and polymer, resulting in an undesirable effect on the membrane performance. Thus, a lot of efforts have been devoted to the functionalization of MWNTs and then the improvement of membrane properties with functionalized MWNTs.

For example, Zheng et al. reported that sulfonated MWNTs with pendant alkyl sulfonic acid groups were synthesized and the resulting TFN membrane exhibits enhanced water flux, surface hydrophilicity, and antifouling ability with the help of sulfonated MWNTs. Zarrabi et al. prepared NH2-functionalized MWNTs and found the TFN nanofiltration membrane using 0.005 wt % NH2-MWNTs as a hydrophilic modifier presented the best separation performance and improved fouling resistance. As reported by Zhao et al., high-flux positively charged nanocomposite NF membranes were developed by uniformly embedding polydopamine-modified MWNTs. However, it is noted that the processing of MWNT functionalization is usually toxic, labor-intensive, time-consuming, and high-cost, and it limits the further development of corresponding TFN membranes.

In this work, we proposed a green, facile, and robust approach to functionalize MWNTs—that is—fast assembly of a tannic acid–FeIII coordination complex coating on the surface of MWNTs. The TFN membrane was then prepared by a conventional interfacial polymerization using trimesoyl chloride (TMC) and piperazine as the organic and aqueous monomers, respectively. To the best of our knowledge, it is the first report to investigate tannic acid–FeIII functionalized MWNTs (TA-MWNTs) and their application in the TFN membrane. Tannic acid (TA), which can be easily obtained from common plants such as oak, green tea, and fruit, is cheap and commercially available. As a kind of plant-derived polyphenol containing sufficient catechol and galloyl groups, TA could readily adhere to the surface of various substrates via covalent and/or noncovalent interactions, and rapidly form a uniform TA–FeIII metal–organic network coating due to the strong chelating ability of TA to iron ions. TA-MWNTs are expected to possess several major advantages as follows. First, the hydrophilic functional groups of TA on MWNTs could help reduce the aggregation of MWNTs and promote its dispersion in the aqueous solution, contributing to the high loading and homogeneous incorporation. Second, the phenol groups of TA could react with acyl chloride groups of TMC and introduce chemical cross-linking polyester bonding to the MWNT–polyamide interface. It is favorable to the compatibility between MWNTs and the polyamide matrix. Third, the chemical stability of TFN membrane would be enhanced, as a result of radical scavenging phenol groups of TA together with the formation of cross-linked polyester bonding between TA and TMC. The properties of a polyamide thin film nanocomposite membrane assisted with TA–FeIII functionalized MWNTs were systematically investigated in terms of water flux, salt rejection, contact angle, long-term stability, antifouling ability, and chlorine resistance.

2. EXPERIMENTAL SECTION

2.1. Materials. The microporous polysulfone (PSI) support film was supplied by the Development Center of Water Treatment Technology (Hangzhou, China). Multiwall carbon nanotubes (MWNTs, purity >95%, OD < 8 nm, length ~30 μm, and –OH content 5.58 wt %) were provided by XFNANO Co., Ltd. (China). Piperazine (PPI) trimesoyl chloride (TMC), tannic acid (TA), iron chloride hexahydrate (FeCl3·6H2O), sodium hypochlorite solution (NaClO, 6–14%), and bovine serum albumin (BSA) were obtained from Aladdin Co., Ltd. Isopropl alcohol (IPA) and cyclohexane were purchased from Xilong Scientific Co., Ltd. (China). Sodium sulfate, sodium hydroxide, sodium dihydrogen phosphate anhydrous, and sodium phosphate dibasic were purchased from Macklin Co., Ltd. All the chemicals were used as received.

2.2. Preparation of Functionalized MWNTs (TA-MWNTs). 0.05 g of MWNTs was dispersed in 50 mL of deionized (DI) water and ultrasonicated for 45 min. 0.5 mL of TA solution (24 mmol/L) was then added, and the suspension was mixed under ultrasonication for 15 min. Subsequently, 0.2 mL of FeCl3 solution (24 mmol/L) was quickly poured, and the whole system was kept under vigorous stirring for 1 min at room temperature. The TA–FeIII functionalized MWNTs (TA-MWNTs) were finally harvested by centrifugation, washing, and freeze-drying.

2.3. Preparation of TFN Membrane. The TA-MWNT/PA TFN membrane was prepared via interfacial polymerization of PIP and TMC on the PSI porous supporting membrane in the presence of TA-MWNTs. First, a certain quality of TA-MWNTs was dispersed into the aqueous phase which consisted of PIP (0.05%), NaOH (0.1%), and IPA (4%). Then the aqueous phase was ultrasonicated for 15 min. The supporting membrane was then immersed into the well-dispersed solution for 5 min. After removal and the draining off of excess solution, the membrane that was absorbed with PIP, and TA-MWNTs were soaked in the organic phase which was composed of TMC (0.05%) in cyclohexane for 30 s to conduct interfacial polymerization. Afterward, the membrane was post-treated at 60 °C for 30 min for further polymerization of the polyamide thin layer. The final membrane was washed with DI water repeatedly and stored in DI water. For comparison, a neat PA TFC membrane and a MWNT/PA TFN membrane were also prepared using the same parameters in absence of TA-MWNTs and in the presence of MWNTs, respectively.

2.4. Characterization. The morphology of the TA-MWNTs was observed by transmission electron microscopes (TEM, JEOL-2100). NETZSCH TG203F3 instrument was employed for thermogravimetric analysis (TGA) of MWNTs and TA-MWNTs at a rate of 10 °C/min from 100 to 800 °C in N2 atmosphere. FTIR spectra were collected by Bruker Alpha with a resolution of 4 cm⁻¹ and 32 scans. The X-ray photoelectron spectroscopy (XPS) spectrum was recorded on a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectroscopy equipped with an Al Ka X-ray source. The surface morphologies of the membrane samples were observed by scanning electron microscopes (SEM ZEISS EVO18 and FE-SEM Zeiss Ultra 55). The dried membrane samples were prepared by coating with a conductive thin layer of sputtered gold. Quantitative surface roughness analysis of the membrane samples was performed by atomic force microscopy (AFM Multimode Nano 4, tapping mode). Contact angles of the membrane samples were determined by OCA15 (Dataphysics Co., Germany) to study the membrane hydrophilicity. At least five different locations were measured to obtain an average value of the contact angle of each membrane.

2.5. Evaluation of Membrane Performance. The pure water flux and salt rejection of the membranes were measured by a lab-scale cross-flow membrane module at an operation pressure of 0.6 MPa at room temperature. The flux (F) was calculated according to eq 1: 

\[ F = \frac{V}{(At)} \]

where V, A, and t presented the total volume of the permeated solution (L), effective membrane area (m²) and operation time (h), respectively. The salt rejection (R) was measured with 5 mmol/L Na2SO4 solution, and deduced by eq 2: 

\[ R = 1 - \left( C_f / C_p \right) \]

where Cf and Cp were the concentrations of the feed and permeation solutions.
respectively. The concentrations of the permeation and feed solutions were determined by electrical conductivity (Mettler Toledo FE38).

Membrane fouling was usually investigated with a mixed solution of salt and organic pollutant. To study the antifouling ability of the PA TFC and TA-MWNT/PA TFN membrane, measurements were periodically carried out to check the changes in the flux and rejection at an operation pressure of 0.6 MPa using Na₂SO₄ (5 mmol/L) and BSA (50 mg/L) mixture as feed solution.

The chlorine resistant capability of the membranes was determined by employing the NaClO solution containing 500 ppm active chlorine. The solutions were placed in darkness and replaced with freshly prepared solutions every 2 days. The membranes were immersed into NaClO solution for a certain time, and then taken out. After being washed by DI water, the membranes were measured in terms of the water flux and Na₂SO₄ rejection.
The long-term test was conducted to study the structure and performance stability of the TA-MWNT/PA TFN membrane. Periodical measurements were carried out to check the permeability and rejection at an operation pressure of 0.6 MPa with 5 mmol/L Na₂SO₄ solution during a period of 50 h.

3. RESULTS AND DISCUSSION

3.1. Characterization of TA-MWNTs. MWNTs were successfully functionalized through a simple and rapid procedure by forming a stable polyphenol–metal complex coating upon the surface. TA, which has ten aromatic rings and a number of hydrophilic hydroxyl groups, may first adsorb onto the MWNT surface and form a monolayer via π–π interaction. And then TA molecules could be further adsorbed through hydrogen bonding and other polar interactions, producing a TA nanolayer on the surface of MWNTs. After the addition of FeCl₃, the thin layer turns to a cross-linked TA–Fe³⁺ coating, as a result of the rigorous complexation of Fe³⁺ and TA. From the TEM images shown in Figure 1, it is visualized that a TA–Fe³⁺ nanolayer (ca. 2 nm) is coated on the outer surface of MWNTs. To further characterize the TA–Fe³⁺ functionalized
MWNTs (TA-MWNTs), XPS, FTIR, and UV−vis absorption spectroscopy were employed. First, XPS analysis was used to study the chemical composition of TA-MWNTs. From Figure 2a, the peaks at 725 and 402 eV are assigned to Fe 2p and N 1s of TA, respectively, and the amount of Fe reaches 0.38%, revealing the presence of the Fe species in TA-MWNTs. The FTIR spectra of MWNTs and TA-MWNTs are shown in Figure 2b. In comparison with MWNTs, an additional peak at \( \sim 1718 \text{ cm}^{-1} \) appears in the TA-MWNT spectrum, indicating the existence of the ester group of TA.24,27 In the UV−vis absorption spectrum of TA-MWNTs (Figure 2c), two peaks are observed at 215 and 274 nm, which are assigned to the \( \pi-\pi^* \) and \( n-\pi^* \) transitions of TA, respectively.29 The photograph in Figure 2d demonstrates the dispersity of MWNTs and TA-MWNTs in aqueous solution. MWNTs and TA-MWNTs are respectively dispersed in DI water by ultrasonication, and then the obtained suspensions are left to stand for 15 min. After standing for 15 min, MWNTs obviously aggregate and precipitate, while TA-MWNTs remain homogeneously dispersed. The rather good dispersity of TA-MWNTs could be attributed to the numerous hydrophilic groups of TA wrapping onto the surface of the MWNTs, and it would further benefit the loading of TA-MWNTs on the TFN membrane and correspondingly the membrane performance.

3.2. Optimization of TFN Membrane. The PA TFN nanofiltration membranes were prepared via conventional interfacial polymerization in the presence of TA-MWNTs, and the schematic diagram for the preparation process of the TFN membrane is demonstrated in Figure 3. TA-MWNTs with concentrations ranging from 0.01% to 0.07% were respectively added into the aqueous phase to obtain TFN membranes with optimized separation properties. The neat PA TFC membrane without TA-MWNTs was also prepared for comparison.

The surface morphologies of TFN membranes with different TA-MWNT concentrations in the aqueous phase were characterized by SEM. From Figure 4, it could be seen that the surfaces of TFN membranes become rougher as some TA-MWNTs appear on the membrane surface, and incremental TA-MWNTs are observed along with the increasing addition of TA-MWNTs in aqueous phase. Furthermore, the TFN membrane with 0.03% TA-MWNT addition presents an abundant and uniform loading of TA-MWNTs, while serious agglomeration of TA-MWNTs is found in the membranes with 0.05% and 0.07% TA-MWNTs. Figure 5 demonstrates the AFM analysis to determine the membrane roughness in terms of the average surface roughness (Ra). As we can observe, the Ra value increases with the addition of TA-MWNTs, suggesting the rougher membrane surface. This is probably due to the immobilization of TA-MWNTs on the membrane surface. These results coincide well with the SEM observation.

The water contact angles of the TFN membranes as a function of TA-MWNT concentrations are shown in Figure 6. The contact angles of the membranes sharply decrease with the increasing TA-MWNT concentration, demonstrating that the incorporation of hydrophilic TA-MWNTs is favorable to the hydrophilicity of the membrane surface. But then the contact angle increases slightly, as a result of the aggregation of high concentration TA-MWNTs (>0.03%).

Figure 7 is a plot of pure water flux and rejection to Na2SO4 vs TA-MWNT concentration in the aqueous phase. Along with the increasing TA-MWNT concentration, the pure water flux continually increases. To be specific, the water flux of the neat PA membrane is 13.3 L/m2h, while the water flux of the TFN membrane with 0.03% TA-MWNTs is 20.2 L/m2h, demonstrating an increase of 51.4%.

Figure 5. AFM images of the surfaces of TFN membranes prepared with different TA-MWNT concentrations in aqueous phase (%): (a) 0.01; (b) 0.03; and (c) 0.07.
membrane goes up to 31.4 L/m²h with 0.03% TA-MWNT addition in aqueous phase. Generally, three main factors are supposed to contribute to the enhancement of water permeability. First, the loading of hydrophilic TA-MWNTs enhances the hydrophilicity of the TFN membrane, leading to the promotion of the hydrogen bond interaction between water molecules and the membrane surface and thus the water transport rate. Second, the dense polyamide chains’ packing is disrupted by the incorporation of TA-MWNTs, introducing more free volume for water molecules passing through. Third, the additional direct water channels could be introduced at the interfacial region between TA-MWNTs and the polyamide, benefiting the low-resistance water transport. Consequently, the water permeation rate increases with the increasing TA-MWNT addition. The chemical bonding, which comes from the reaction between the phenol groups of TA and the acyl chloride groups of TMC, contributing to the compatibility of TA-MWNTs and the polyamide matrix. Thus, the structure and property stability of the membrane are expected to be enhanced. But when the TA-MWNT concentration is larger than 0.03%, the Na₂SO₄ rejection seriously drops, even down to 70%, because nonselective defects are inevitably generated by the macroscale aggregation of TA-MWNTs. The analysis coincides well with the results of SEM and contact angles. On the basis of the results above, the TFN membrane prepared with 0.03% TA-MWNT concentration is considered to possess the best overall separation properties, that is, the optimal water flux and Na₂SO₄ rejection.

3.3. Characterization of TFN Membranes. To get deep insight into the performance improvement brought by TA-MWNTs, the optimized TA-MWNT/PA TFN membrane was further characterized. Figure 8 presents the FESEM image of the surface of the TA-MWNT/PA TFN membrane with higher magnification. It could be clearly observed that TA-MWNTs are well incorporated into the surface or are partly imbedded into the top layer. The polyester bonding could be formed due to the reaction between the phenol groups of TA and the acyl chloride groups of TMC, contributing to the compatibility of TA-MWNTs and the polyamide matrix. Thus, the structure and property stability of the membrane are expected to be enhanced.

The structure stability and long-term durability are of great importance to membrane application. In particular, it is a critical issue for the TFN membrane incorporated with inorganic fillers, because nanofillers may leak out if the compatibility and bonding are not good enough. So a long-term measurement was performed, and the results are shown in Figure 9. It can be found that the TA-MWNT/PA TFN membrane presents good long-term stability, serving as a proof of the optimal design.

Figure 6. Contact angles of the TFN membranes prepared with different TA-MWNT concentrations in aqueous phase.

Figure 7. Effect of TA-MWNT concentrations on the pure water flux and Na₂SO₄ rejection of TFN membranes.

Figure 8. FESEM image of the surface of TA-MWNT/PA TFN membrane.

Figure 9. Long-term stability of TA-MWNT/PA TFN membrane.
of the strong chemical bonding and good compatibility between TA-MWNTs and the polyamide matrix.

The membrane fouling resistance test was conducted using the mixture of Na₂SO₄ and BSA to simulate the real operational environment. The changes in flux and rejection of PA and TA-MWNT/PA membranes during an operation time of 25 h are illustrated in Figure 10. The fluxes of both membranes drop at the first 10 h, and then reach a relatively stable state. Both rejections slightly increase due to the blockage of salt transport brought by the adsorption of BSA on the membrane surface. After 25 h of filtration, the flux of the PA membrane severely declines to only \(\sim 56\%\) of its original flux, while the TA-MWNT/PA membrane retains as high as \(\sim 80\%\) of the original flux. The significantly improved antifouling ability of the TA-MWNT/PA membrane could be ascribed to the enhanced hydrophilicity of the membrane surface incorporated with hydrophilic TA-MWNTs. The hydrophilic surface of the membrane could help to weaken the hydrophobic interaction and reduce the protein adsorption.

During the practical operation and cleaning process, the membrane is inevitably exposed to oxidation and chemical reagent solutions, so the antioxidation capability is also crucial to the service lifespan of the membrane. Sodium hypochlorite (NaClO), which is commonly used in the disinfection process of the NF membrane, is employed as the active chlorine agent for the determination of oxidation durability in this study. The water flux and Na₂SO₄ rejection of PA and TA-MWNT/PA membranes were measured after immersion in NaClO solution with 500 ppm active chlorine for a certain time. The PA membrane is known to be easily degraded by chlorine exposure because aromatic rings bonded to N–H group of amide linkage are sensitive to the attack of chlorine radical. As shown in Figure 11, only after 9000 ppm h of chlorine exposure, the rejection of PA membrane obviously drops down, because hypochlorite could diffuse into the polyamide layer and bring about the cleavage of the amide groups. At the same time, the water flux gradually increases with the increasing immersion time. Compared with the PA membrane, the TA-MWNT/PA membrane presents a remarkable enhancement of chlorine resistance. During the whole NaClO immersion treatment, the water flux of TA-MWNT/PA membrane decreases at first and then goes up. The –OH groups in the ortho positions of polyphenol TA could be oxidized into orthoquinone in NaClO solution. So –OH groups are consumed, and the hydrophilicity of the membrane decreases, leading to a decreased water flux. But some damage of the amide linkages may appear after a long time of NaClO exposure, and the water flux increases afterward. It is worth noting that the rejection of the TA-MWNT/PA membrane only presents an acceptable decline after a chlorine exposure as high as 252 000 ppm h. This phenomenon could be explained as follows. On the one hand, the radical capturing capability of the phenol groups of TA could help to protect polyamide from chlorine radical attack, which has been proven in the previous literature. On the other hand, the additional cross-linked structure is produced by the interaction between phenol groups of TA and acyl chloride groups of TMC. The formation of polyester bonding could benefit the TFN membrane’s stability against chlorine, because it is more stable than polyamide when exposed to active chlorine. Thus, with the aid of TA-MWNTs, the PA TFN membrane possesses an enhanced chemical stability and oxidation resistant capability.

3.4. Comparison. To fully reveal the advantages of the improvement of membrane properties assisted by TA-MWNTs, the performance of three kinds of membranes including PA, MWNT/PA, and TA-MWNT/PA TFN membranes are summarized and compared in Figures 12 and 13.

Figure 12 exhibits the pure water flux and Na₂SO₄ rejection of three membranes. It is found that both MWNT/PA and TA-MWNT/PA TFN membranes have higher water permeation rates, and present different degrees of rejection reduction, in comparison with the neat PA membrane. The TA-MWNT/PA membrane possesses the highest water flux because of the loading of the fairly hydrophilic TA-MWNTs. While the rejection of the MWNTs/PA membrane reduces to 67%, the TA-MWNT/PA membrane still maintains at an acceptable rejection rate. It could be attributed to the chemical bonding and good compatibility between TA-MWNTs and the PA matrix. Moreover, from Figure 13, the TA-MWNT/PA membrane exhibits a significantly improved hydrophilicity among these membranes. Therefore, the TFN membrane could obtain a prominent improvement of properties by the assistance of TA-MWNTs.
and MWNTs/PA membranes, the TA-MWNT/PA TFN membrane displays a prominent improvement of properties.

4. CONCLUSIONS

MWNTs were functionalized through a simple and robust formation of a stable tannic–Fe(III) complex coating upon the surface. The functionalized MWNTs (TA-MWNTs) present a good dispersity in the aqueous solution due to the numerous hydrophilic groups of TA. The polyamide (PA) thin film nanocomposite (TFN) membrane was then constructed by interfacial polymerization in the presence of TA-MWNTs. The effect of different TA-MWNT concentrations on membrane morphologies and properties were investigated. When 0.03% of TA-MWNTs were added, the water flux of the TFN membrane was found to reach 31.4 L/m²h, which was 2.36 times that of the neat PA membrane, while Na₂SO₄ rejection was well retained. This is due to the good loading of hydrophilic TA-MWNTs and favorable chemical bonding between TA-MWNTs and the polyamide matrix. The TFN membrane exhibits an enhanced antifouling ability and good long-term stability. It is worth noting that the TFN membrane also possesses an excellent chemical stability and oxidation resistant capability, as a result of the radical capturing capability of phenol groups of TA as well as more stable polyester bonding produced by the interaction between the phenol groups of TA and the acyl chloride groups of TMC. Compared with the PA

**REFERENCES**


(22) Ejima, H.; Richardson, J. J.; Liang, K.; Best, J. P.; van Kooiwerden, M. P.; Such, G. K.; Cui, J. W.; Caruso, F. One-Step Assembly of Coordination Complexes for Versatile Film and Particle Engineering. Science 2013, 341 (6142), 154–157.


