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A DNA-mimic contact-active functional group for antifouling ultrafiltration membranes

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ABSTRACT: Despite advanced materials and techniques to reduce the fouling issue of membranes, 10~30% of the cost of ultrafiltration (UF) processes have been spent on membrane cleaning. Particularly in water treatment, the traditional heavy metal-based method is challenged due to its environmental pollution risk and increasing public health awareness. Here, we report the synthesis of a metal-free contact-active antifouling and antimicrobial membrane by covalently functionalizing a commercial polyacrylonitril (PAN) UF membrane with 2,4-diamino-1,3,5-triazine (DAT) via a one-step catalyst-free hydrothermal [4+2] cyclization of dicyandiamide reaction. The proposed mechanism of the antimicrobial activity of the DAT-functionalized membrane is through strong attraction between the DAT groups and the microbial membrane protein via strong hydrogen bonding, leading to microbial membrane disruption and thus microbe death. A high water flux and good reusability of the membrane against protein in a UF experiment were achieved. The low cost, easy availability of the compounds, as well as the facile reaction offer a high potential of the membrane for real applications in ultrafiltration.

1. Introduction

Energy-saving membrane separation has been of much interest in recent years in water purification, pharmaceutical, biotechnological and food industries (Baker et al., 1991; Visvanathan et al., 2000; Zhong et al., 2015). A major challenge in the ultrafiltration (UF) process that needs to be addressed is membrane fouling by microbial and other biomolecules in the feed stream, which causes flux decline, energy consumption increase and membrane lifetime shortening (Asatekin et al., 2007). Aggressive chemicals and additional operating cost are required to remove the foulants. Typically, about 10-30% cost of a UF process is spent on membrane cleaning (Noble and Stern, 1995; Asatekin et al., 2007). Novel membranes with antimicrobial property are certainly attractive from this perspective (Ahmed et al., 2013; Mukherjee and De, 2018). One common approach is to introduce a second agent with antibacterial properties into the membrane, such as N-halamine polymers (Hui and Debiemme-Chouvy, 2013), heavy metal nanoparticles (particularly silver nanoparticles, AgNPs) (Yu et al., 2003), SWNTs (Ahmed et al., 2012), polyzwitterions and enzymes (Vaterrodt et al., 2016). However, this approach suffered from material leaching which caused not only a high risk of heavy metal or enzyme contamination to the surrounding environment, but also loss of the antibacterial properties (Liu et al., 2015; Ghobadi et al., 2016). With increasing environmental and public health awareness, there is an emerging requirement to develop antibacterial membranes without additives (Wang and Wang, 2011; Wang et al., 2015; Wang et al., 2017b). Among this effort, polymer membranes functionalized by quaternary ammonium salt (QAC) such as poly(4-vinyl-N-methylpyridinium iodide) (P4VMP) and dimethyldecylammonium chitosan-graft-poly(ethylene glycol) methacrylate (DMDC-Q-g-EM) have been studied intensively in recent years due to their efficient antimicrobial property (Fuchs and Tiller, 2006; Waschinski et al., 2008; Li et al., 2011; Zhang et al., 2016), which is based on the strong electrostatic interactions between the positively charged ammonium group and the negatively charged lipid bilayer of the microbial membrane that leads to membrane disruption and thus microbe death (Li et al., 2011; Zhang et al., 2016). However, most of the QAC functionalized polymers are water soluble, and the membranes are not permeable to water, which hindered their application in water treatments. Moreover, the synthesis of QACs typically needs multiple steps and expensive reagents. In principal, any local strong interaction with the cell membrane may induce cell death. Such a contact-active microbicidal concept (Li et al., 2011) is meaningful and inspired us to find other functional groups rather than cations that could form strong interactions with microbial membrane proteins.

We previously developed a method to introduce 2,4-diamino-1,3,5-triazine (DAT) functional groups into a polymer with intrinsic porosity *via* a catalyst-free [4+2]-cycloaddition reaction of dicyandiamide (DCD) and nitrile groups in PIM-1 (Wang et al., 2017a). The DAT group is a mimic of DNA bases and is known to self-associate reliably by forming hydrogen-bonded motifs I-III (Figure 1, a and b) (Malek et al., 2005). The bioactivity of small DAT-containing molecules has been studied extensively in biochemistry (Janssen et al., 2007; Janssen et al., 2008; Zhou et al., 2015) and pharmaceutical chemistry (Menicagli et al., 2004; Sączewski et al., 2006). The existence of multiple hydrogen bonds in DAT functional groups suggests a strong interaction with cell membrane is possible, and thus stimulate us to study its potential as a novel contact-active microbicide to control membrane fouling. Polyacrylo-

nitrile (PAN) is one of the most widely used UF membranes owing to its good solvent resistance, high chemical stability, excellent mechanical strength, low cost, and superior thermal stability (Chen et al., 2013; Liu et al., 2015). In this work, the easily available PAN material rich in nitrile groups was chosen as a model substrate to illustrate our concept of the strong hydrogen-bond induced contact active property.

Figure 1. DNA-base mimic of DAT functionalization and the synthesis of DATPAN. (a) DNA structure, and the strong hydrogen bonding interaction between DNA bases. (b) Synthetic scheme for chemical functionalization of PAN to DATPAN, and three types of hydrogen bonds between DAT groups.

2. Experimental

2.1 Chemicals and reagents

Polyacrylonitrile (PAN) polymer powder was used as obtained from Sigma-Aldrich with an average molecular weight 150K. The PAN membrane was supplied by Kelheim Fibers GmbH, Germany. Dicyandiamide, 2-methoxyethanol, potassium hydroxide (KOH), and sodium chloride (NaCl) were received from Sigma-Aldrich and used without further treatment. Deionized water (DI) water purified with a MilliQ System (Millipore, Inc.) was used in this research.

2.2 Functionalization of PAN membrane

The functionalization of PAN powder was carried out as follows: 0.5 g PAN powder mixed with 2.0 g dicyandiamide and 0.2 g KOH was added to 60 ml 2-methoxyethanol in a 100 ml autoclave, which was then sealed and heated in an oven at 160 °C for 5 hours. After cooling, the obtained powder of a brown colour, named p-DATPAN, was taken out and washed vigorously with hot DI water to remove unreacted dicyandiamide and then dried in a vacuum oven overnight at 100 °C. This product was used for NMR and IR characterization to confirm the functionalized chemical structure.

The PAN membrane with a 5×5 cm² surface area was immersed into 60 ml 2-methoxyethanol in a 100 ml autoclave containing 500 mg dicyandiamide and 50 mg KOH. The autoclave was then sealed and heated in an oven at 160 °C for 5 hours. After cooling, the obtained membrane, named as DATPAN, was taken out and washed thoroughly with hot DI water to remove unreacted dicyandiamide. Some DATPAN membranes were dried in a vacuum oven at 80 °C for characterization purposes, and others were stored in DI water for further utilization. The DATPAN was found to be brittle when dried but good in strength when wet.

2.3 Analytical

All nuclear magnetic resonance spectroscopy (NMR) spectra were recorded on a Bruker 900 MHz AVANACIII NMR spectrometer equipped with a 4 mm Bruker MAS probe (BrukerBioSpin, Rheinstetten, Germany). The spectra were recorded under a 12 kHz spinning rate using a CP pulse program with 5 ms contact time. To achieve a good signal-to-noise ratio, the spectra were recorded by collecting 48 k scans with a recycle delay time of 2 s. The Bruker Topspin 3.2 software (Bruker BioSpin, Rheinstetten, Germany) was used to collect and analyse data. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet iS10 Smart FTIR spectrometer (Thermo Scientific, USA) with a Smart OMNI Transmission, ranging from 4000 cm^{-1} to 550 cm^{-1} . Scanning electron microscope (SEM) images were obtained on a Nova nano SEM operated at an accelerating voltage of 5 kV; samples were sputtering coated with 4-nm-thick Ir prior to observation. A Dimension Icon SPM (Bruker) was used to obtain the topography images and the roughness of the membrane surface in the tapping mode. Atomic force microscopy (AFM) probes (FESPA-V2, Bruker) with a spring constant of 2.8 N/m were employed for the measurement. The scanning speed was 1 Hz.

2.4 Determination of separation performance

The pure water permeability of membranes was measured as follows: A dead-end high pressure stirred cell kit (Sterlitech HP4750) with a volume of 300 ml and an active membrane area of 14.6 cm^2 pressurized with nitrogen gas was used. DI water was selected as a feed solution. The membrane samples were soaked in DI water and compacted at 0.5 bar for 30 min to reach a steady state prior to the measurements. Afterwards, the water flux was measured at pressures ranging from 0.5 to 5.0 bar. The water flux (J) and water permeability (P) was calculated as follows:

$$J = \frac{V}{A\Delta t} \quad (1)$$

$$P = \frac{J}{\Delta p} \quad (2)$$

where V is the volume of permeated water (L), A is the effective membrane area of the membrane (m^2), Δt is the permeation time (h), and Δp is the applied pressure (bar).

Bovine serum albumin (BSA, 1 g/L aqueous solution) was used as a model protein foulant in this study for biofouling investigations. The permeability performance was measured using the same cell kit as abovementioned, but with the feed pressure fixed at 2.5 bar. The permeate solution was collected every minute and weighed to calculate the flux (J) and permeability (P) using equations (1) and (2). The concentration of BSA in the permeate solution (C) was monitored by UV-Vis, and the rejection rate (R_s) was calculated as follows:

$$R_s = \frac{C_0 - C}{C_0} \quad (3)$$

where C_0 is the BSA concentration in feed solution and C is the concentration in the permeate.

To evaluate the antifouling property of the membranes, the flux recovery ratio (FRR) was calculated after each cycle of the fouling test where the fouled membrane will be cleaned by backwashing with 500 ml deionized water. The FRR was calculated using the equation:

$$FRR = \frac{J_R}{J_0} \times 100\% \quad (4)$$

Where J_0 is the pure water flux before fouling test and J_R is the pure water flux after fouling.

2.5 Determination of antibacterial properties

E. coli DSM 1103 was used to evaluate antibacterial efficiency. The methods and conditions were as described previously, but with minor modifications.(Duong et al., 2015; Villalobos et al., 2016) In brief, a single colony of *E. coli* DSM 1103 was inoculated into 20 ml LB Broth (Lennox) (Sigma-Aldrich, St. Louis, MO, USA) and incubated in a shaker incubator set at 200 rpm and 37 °C for 17 h. The bacterial culture was then diluted with 0.85% w/v NaCl to an OD600 of 0.07. This OD measurement at a 600 nm wavelength corresponds to an approximate cell density of 107 cells/mL. Prior to the experiment, membranes were cut aseptically into 2 cm × 2 cm sections by sterile scissors and were immersed into 10 ml diluted *E. coli* DSM 1103 cell suspension. Three replicates were prepared for each membrane. The cell suspensions containing the membranes were then incubated in a 200 rpm shaker incubator at 37 °C for 24 h. After that, the membranes were removed from the cell suspensions with sterilized tweezers, gently washed with 6 ml 0.85% w/v NaCl and then placed into individual tubes that contain 2 ml 0.85% w/v NaCl. The tubes were then ultrasonicated for 3 min by a Q500 sonicator (Qsonica) at 25% amplitude to dislodge the attached bacteria into the suspension. The dislodged bacterial cell suspensions were diluted 2000-fold with 0.85% w/v NaCl. A 2X LIVE/DEAD BacLight Bacterial Viability Kit (Thermo Fisher Scientific, MA, US) was used to stain the bacteria prior to counting live cells by flow cytometry on an Accuri C6 (BD Bioscience, NJ, US). The attached bacterial cells on the membrane surfaces were also observed under an FESEM after fixing the cells with 4% w/v paraformaldehyde solution. The antibacterial efficiency (E_b) was represented by eqn (5):(Liu et al., 2015)

$$E_b = (W_1 - W_2) \times 100\% \quad (5)$$

where W_1 and W_2 are the percent of broken cells of *E. coli* corresponding to PAN (as a blank sample) and DATPAN, respectively.

3. Results and discussion

3.1 Characterization of DATPAN

Prior to membrane fabrication, the reaction was first conducted on polyacrylonitrile powder (p-PAN, p indicates that the material is powder), and the product was named p-DATPAN. The p-PAN and p-DATPAN were subjected to solid NMR analysis, and the ^{13}C spectra are shown in Figure 2. Two characteristic peaks at 30 and 121 ppm were assigned to the aliphatic carbon and carbon in nitrile (CN) groups. After modification, the CN groups were transformed to DAT; the carbon signal at 121 ppm disappeared, and two new peaks at 180 and 167 ppm appeared, accordingly belonging to the sp^2 carbons in the triazine ring, which is consistent with the result observed in liquid NMR analysis of the transformation from PIM-1 to DATPIM (Wang et al., 2017a).

The DATPAN membrane was obtained via the same reaction as the PAN membrane. FT-IR analysis was conducted on both the powder and membrane form to determine the functional groups present in the material. As shown in Figure 3a and 3b, the characteristic peaks in virgin polyacrylonitrile at 2930, 2243, and 1470 cm^{-1} were attributed to the stretching vibration band of methylene ($-\text{CH}_2-$), stretching vibration band of nitriles ($-\text{CN}-$), and bending vibration band of methylene ($-\text{CH}_2-$), respectively. The disappearance of the CN vibration peak at 2243 cm^{-1} in Figure 3c and 3d clearly demonstrated the successful transformation of the nitrile groups, while the wide new peaks in the region of 3000-3700 cm^{-1} indicated strong hydrogen bonds in the product.

Figure 2. Solid ^{13}C NMR spectra of PAN and DATPAN powder

Figure 3. FT-IR spectra of PAN and DATPAN powder (p-) and membranes; the insert shows a prepared DATPAN membrane. XPS analysis was used to determine the fractions of the parent PAN membrane as well as the modified membrane of DATPAN in the near surface region. (Huang et al., 2018) As shown in Figure 4, the C 1s peak obtained for PAN was fitted with two peaks. The highest peak, labelled (a) in the figure, was centred at 286.5 ± 0.2 eV, corresponding to the CH and CN carbons of PAN (Asatekin et al., 2007). The second peak (b) at 285.2 ± 0.2 eV may be attributed to the CH_2 carbons of the PAN chains. For DATPAN, the whole peaks became broader, and a third peak was better fitted at 287.0 ± 0.2 eV, as marked (f), corresponding to the sp^2 carbons in the triazine rings. Only one sharp peak centred at 399.5 ± 0.2 eV was observed in the N 1s XPS spectrum of PAN, representing the

nitrile groups. DATPAN, however, gave two peaks at 399.3 and 398.1 $\pm$ 0.2 eV, corresponding, respectively, to the nitrogen in
triazine rings and the free amine groups thereof. The XPS spectra further confirmed the successful transformation of nitriles in PAN
to diamine-triazine in DATPAN.

Figure 4. XPS high-resolution C 1s and N 1s spectra of the parent PAN and DATPAN membrane selective layer surfaces and representative fit.

The SEM images of PAN and DATPAN surface are shown in Figure 5a and 5e, respectively. The PAN membrane has a uniform microporous structure with a pore size diameter of approximately 20~60 nm. The surface pore size and porosity of the DATPAN membrane (Figure 5c) are quite similar to those of the PAN membrane, which indicates that the microporous structure of the skin layer was preserved. Figure 5b and 5f show the cross-sectional SEM micrographs of the PAN and DATPAN membranes, respectively. It is difficult to distinguish the top skin layer in both membranes, which can be as thin as 0.5-3 nm, as reported. (Xu et al., 2012) The PAN membrane presents a typical “network like” structure under the skin layer. Interestingly, a second layer approximately 2 μ m thick can be seen between the top layer and the bulk in the DATPAN membrane, indicating that the group transformation reaction occurred asymmetrically by depth. Elemental mapping for carbon and nitrogen showed uniform dispersion of both elements in both materials, while a much stronger nitrogen signal intensity in DATPAN was observed, which is consistent with the higher N content in DATPAN. Since the transformation occurred in the solid-liquid interface, the skin layer of the porous membrane reacted faster to transform the -CN groups into DAT groups, which made the skin denser because of the strong hydrogen bond between the DAT groups. As a result, the skin layer reflects the interface between the inside membrane and the liquid phase. The pore size and pore size distribution after transformation became smaller, as seen from the cross-section SEM images, because of the strong hydrogen bond between DAT groups.

Figure 5. SEM (a-h) and AFM (i-l) images of membranes: (a) PAN surface, (b) PAN cross-section, (c) C mapping of (b), and (d) N mapping of (b); (e) DATPAN surface, (f) DATPAN cross-section, (g) C mapping of (f), and (h) N mapping of (f). (i, g) AFM of PAN, surface roughness 2.46 nm, and (k, l) AFM of DATPAN, surface roughness 2.41 nm.

The membrane surface roughness was measured by AFM and is illustrated in Figure 5 (i-l). It can be seen that the original PAN membrane has a uniform surface with a root-mean-square surface roughness (Ra) of 2.46 nm. When the CN groups were transformed to DAT, a relatively more homogeneous surface was observed, and the Ra value decreased to 2.41 nm. In general, a smooth hydrophilic surface is beneficial for antifouling.(Deng et al., 2008) It is worth noting that normally, the membrane surface become rougher after surface modification (Tang et al., 2007; Qiu et al., 2011). The more homogeneous surface in DATPAN may be explained by the fact that the surface polymer chains of DATPAN were cross-linked through hydrogen bonding.

3.2 Antibacterial performance of DATPAN membrane

Most biochemical properties of membranes are dependent on the chemical structure of the surface (Hou et al., 2009). In addition to morphological structure changes, the chemically modified DATPAN membrane containing the bio-active DAT groups was expected to show different biochemical properties. Antimicrobial activities of the purely organic constructed film DATPAN against *E. coli* were evaluated using DSM 1103. The experiment was designed to evaluate the resistance of non-leaching antimicrobial-treated specimens to the growth of microbes under dynamic contact conditions. The antibacterial performance of the DATPAN membrane was evaluated through a comparison with the bare PAN membrane regarding the (i) amount of bacteria attached to the surface of the membranes and (ii) bacterial growth inhibition of the suspended plus attached bacteria (Duong et al., 2015). The FESEM images of membrane surfaces after treatment with an *E. coli* solution are displayed in Figure 6. It can be seen that more *E. coli* cells are attached on the PAN membrane surface (Figure 6a), while almost no intact cells can be observed on the DATPAN film surface. Additionally, some spots similar to those observed in the literature (Li et al., 2011) and assigned to fragments of disrupted cells could be observed (Figure 6b), indicating substrate-induced cell disruption and death. A clear surface of the membrane after bacteria contact may be caused by two factors: (1) the morphological structure change of the film surface, particularly the hydrated ultrathin layer formed by the strong interaction between the DAT groups of the film and water molecules, decreased surface

adsorption, and (2) the bacterial growth was inhibited by the DATPAN compound, which resulted in a low cell population of the whole system. The total bacterial growth inhibition activity was then evaluated by a viable cell counting technique. The result is presented in Figure 6c as relative cell viability, which is defined as the percentage of viable suspended and attached bacterial cells for the DATPAN support sample relative to those for the bare PAN support sample. Only 26% cell viability remained in the sample with DATPAN support compared with the sample with PAN support, further evidencing the antibacterial activity of the DATPAN membrane.

Figure 6. Bacterial adhesion on (a) the bare PAN and (b) DATPAN membranes, and (c) growth inhibition of suspended + attached bacteria after membrane exposure to *E. coli* DSM 1103 for 24 h. The red-oval marked spots in (b) are magnified and shown on the right, accordingly.

3.3 Performance in water ultrafiltration with and without fouling agents

Changes in the selective layer morphology and chemistry after chemical transformation might be expected to influence the water contact angle and the pure water flux. The hydrophilicities of the parent PAN and DATPAN membranes were measured and compared in Figure 7. Both membranes showed high hydrophilicity with water contact angles of 25° and 38°, respectively. The slight increase in the contact angle of DATPAN may be attributed to the flatter surface morphology. High hydrophilicity facilitates a stronger affinity between the membranes and water (Duong et al., 2015). As shown in Figure 7, the water flux of both the pristine PAN and DATPAN were increasing linearly with the increase of pressure and no obvious decrease in flux could be observed after the modification, particularly at lower pressure. The retentive water flux indicates that the pores after functionalization were not changed too much.

Figure 7. Surface contact angle and water fluxes of PAN and DATPAN membranes.

Figure 8. Water flux of the membrane during filtration of 1.0 g/l BSA suspension operated at 2.5 bar.

One limitation for the application of contact-active antimicrobial surfaces is that they can be masked easily by conditioning films from organic compounds, such as protein originally in solution or from dead cells, resulting in a mass decrease of permeability. The flat surface, together with the SEM observation of a clean surface after microbial contact, suggest good activity against protein fouling of the DATPAN film. To evaluate the anti-protein-fouling property of DATPAN, a dead-end membrane ultrafiltration system was used with 1.0 g/l BSA/water suspension as the feed solution. As shown in Figure 8, the flux decreased dramatically by about 40% in the initial 1 hour for both PAN and DATPAN membranes, after which, the water flux with DATPAN membrane was almost constant while kept decreasing when PAN membrane was applied. The protein molecules in the feed deposit or adsorb on the membrane surface, forming a thin dense protein layer (biofilm formation), which is proposed as the reason for the drop in flux in the first few minutes of operation (Stafie et al., 2004; Yu et al., 2013; Liu et al., 2015). Tested membranes were then cleaned by backwashing with 500 ml deionized water, and re-challenged with 1.0 g/l BSA/water suspension for the next run. The flux recovery ratio (FRR) was analysed with the first point of each cycle, and FRR values of 85.7%, 79.2%, 77.8% for PAN, and 91.7%, 87.9%, 86.5 for DATPAN were obtained for the first three recovery cycles, respectively. The higher FRR values of DATPAN suggest the fouling layer on DATPAN membrane is relatively loose and easily removable. Interestingly, there was no big drop in flux after three cycles when steady state was achieved using DATPAN membrane (10 LMH or 5.8%), however, a significant decrease when PAN membrane was used (54 LMH or 33%). This result suggest the fouling layer on DATPAN might protected the membrane from further fouling, arguably because of the flatter surface and hydrogen bonding interaction between DAT groups and protein, by

inhibiting more protein going inside. Easy cleaning and high FRR undoubtedly will benefit the real applications in water ultrafiltration by reducing the cost.

3.4 Mechanism proposal of microbe death

A plausible mechanism of the DATPAN-induced microbe cell death was proposed and schematically illustrated in Figure 9. It is well known that lipid and protein are the two main contents of the microbe cell membrane. For the QAC-based contact-active antimicrobial materials, the electrical force between the polymer cationic surface and anion lipid may tear the cell membrane, which may cause membrane disruption and cell death. In the case of DATPAN, there are many DAT groups functionalized on the surface that may form hydrogen bonds with the protein of the cell membrane. Similar to the cation-anion interactions, such strong hydrogen bonding may provide a driving force to disrupt the cell membrane and induce microbe cell death as a result. What should be mentioned is that the hydrogen bond interaction is a dynamic equilibrium, which makes it easier to remove under solvent conditions.

Figure 9. Schematic diagram of the hydrogen bond interaction between the DAT groups on the DATPAN membrane surface and the peptide in protein, which may induce microbe cell membrane disruption and microbe death.

4. Summary and conclusions

For the first time, the widely used antibacterial small molecular structure of DAT was applied to an ultrafiltration membrane with metal-free antimicrobial activities along with high water flux. The surface morphology and chemical structure of the DATPAN were well characterized, which gave us a better understanding of the structure-activity relationship. Hydrogen bonding between DAT and the microbe cell membrane that induced cell membrane disruption and microbe death was proposed. The metal-free membrane prepared with low cost, easily available and simple operations revealed good antibacterial and antifouling performance, showing high potential for applications beyond water purification or the fractionation of proteins. This study also provides a new strategy for the development of metal-free antimicrobial materials.

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Highlights:

- A DNA-mimic group DAT is used as a novel antimicrobial agent
- A DAT-PAN UF membrane is prepared by an easy surface reaction
- The DAT-PAN membrane showed contact-active anti-biofouling
- Novel contact active model of hydrogen bonding is proposed
- High flux recovery ratio is obtained