Journal of Membrane Science 528 (2017) 1–11

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Cell membrane mimetic coating immobilized by mussel-inspired adhesion on commercial ultrafiltration membrane to enhance antifouling performance

Qi Xue, Hao Cao, Fanning Meng, Miao Quan, Yong-Kuan Gong*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry, of Education, College of Chemistry and Materials Science, Northwest University, Xian 710127, Shaanxi, China

ARTICLE INFO

Keywords:
Ultrafiltration membrane
Antifouling
Phosphorylcholine
Bioadhesion
Polydopamine

ABSTRACT

A facile method of modifying commercial polyethersulfone ultrafiltration membrane (PESUM) was developed based on mussel adhesive mimetic polydopamine (PDA) and cell membrane antifouling phosphorylcholine (PC). The PESUM was firstly coated with a thin PDA layer to confer the membrane adhesive property. A cell membrane mimetic and mussel adhesive mimetic random copolymer (PMEND) bearing both antifouling PC zwitterions and adhesive dopamine groups at different side chains was then immobilized onto the PDA surface by dopamine adhesion from the aqueous solution. The immobilized PMEND spontaneously formed a cell outer membrane mimetic film on the PESUM/PDA surface, which was stable in air, gasoline and pH 3–10 water for more than 2-weeks. Importantly, the water flux of this PESUM/PDA/PMEND membrane could be recovered up to 100% and 93% after one and three cycles of fouling by 1.0 mg/mL BSA solution ultrafiltration, respectively. More importantly, the modified membrane could remove more than 99.99% of oil from an 80,000 ppm gasoline/water emulsion. Furthermore, this PDA mediated cell outer membrane mimetic modification strategy is substrate independent and can be applied to other membranes and surfaces to enhance antifouling performance.

1. Introduction

Membrane fouling is a severe problem in pressure-driven separation processes such as reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. It hampers the successful applications of membrane technologies by diminishing the separation performance and shortening the service life of membrane modules [1–5]. The fouling is caused by the attachment of foulants (including inorganic, organic, and biological substances) on membrane surfaces. Protein adsorption and microbial cell adhesion are the main source of biofouling, which may account for 50–90% of the fouling and are difficult to eradicate from the membrane, since microorganism can grow, multiply and relocate on the membrane surface to form a mature biofilm with a few initial colonies [3,6–8].

It is generally accepted that the antifouling performance can be enhanced by increase the surface hydrophilicity because protein and many other foulants are hydrophobic in nature [9–11]. Thus, hydrophilic polymers such as poly(ethylene glycol) (PEG) and zwitterionic polymers were extensively applied in membrane research to improve biofouling resistance. PEGylation of membrane surfaces could significantly increase the hydrophilicity and antifouling performance [12–14]. However, reports have shown that PEG degrades by oxidation, especially in complex media, may not suitable for long-term use [15,16]. Alternatively, zwitterionic polymers such as poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC), poly(carboxybetaine methacrylate) (PCBMA), poly(sulfobetaine methacrylate) (PSBMA) and poly(amino acid), all exhibit remarkable antifouling properties under mild conditions and have been proven to be excellent candidates as nonfouling materials due to their strong hydration capacity contributed by high density of the zwitterions via electrostatic interactions [17–22].

On the other hand, the zwitterionic feature of paired positive and negative charges of PCBMA and poly (amino acid) is easily changed to positively charged, when used in acidic pH. Thus the adhesion of negatively charged biomolecules and cells are enhanced due to the electrostatic attraction. In comparison, the phosphorylcholine (PC) zwitterions in cell membrane can resist the pH change in the body (pH 4–10) and maintain perfect fouling resistance. The excellent antifouling performance of PC zwitterion can be attributed to its strongly adsorbed water molecules. Morisaku reveals that about 23 H_2O molecules were associated to each PC repeat unit in PMPC polymer

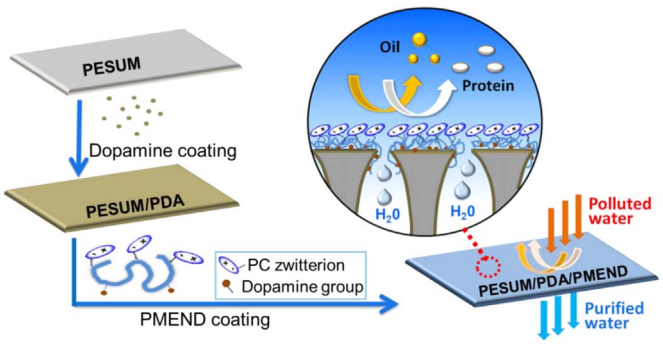
* Corresponding author.
E-mail address: gongyk@nwu.edu.cn (Y.-K. Gong).

http://dx.doi.org/10.1016/j.memsci.2017.01.009
Received 20 October 2016; Received in revised form 6 January 2017; Accepted 6 January 2017
Available online 11 January 2017

by thermal analysis [23]. In contrast, the associated water molecules with sulfonate and amino or quaternary ammonium groups on polyelectrolytes is about 4, and that with one sulfobetaine zwitterion is 7 ± 1 [24,25]. This number of combined water molecules per group is lower than 80% of that found by Murphy et al. for a PC zwitterionic copolymer [26]. The associated water layer of the PC coating is so strong that prevents the adhesion of foulants by both steric hindrance and energy barrier, which result in ultralow fouling of less than 5 ng/cm^2 [21,27]. However, it is difficult to apply such a strongly hydrophilic zwitterion polymer on hydrophobic membranes due to incompatibility of the materials [5]. Furthermore, all the reported applications of PC coatings in the membrane modification are grafted polymer brushes via multistep process under harsh reaction conditions, which make it a great challenge to apply in large scale [17,28–31].

Inspired by the universal adhesion of marine mussels in wet and turbulent environments, Messersmith and his colleagues developed a polydopamine (PDA) strategy for multifunctional coatings on a variety of materials [32]. Although the exact polymerization and interaction mechanism of PDA remains elusive, there is a general acceptance that the mussel-inspired coating protocol involves an oxidative polymerization process [33–35], which needs to be initiated by an oxidization reaction [32,34,35]. Moreover, the catechol group plays the central role in such mussel-mimicking versatility [32]. By introducing the bioadhesion mimetic catechol groups at some side chains of a cell membrane phosphorylcholine mimetic copolymer (PMNC), we have successfully immobilized the catecholic phosphorylcholine copolymer on substrate independent surfaces by simple dip-coating in the aqueous solution [36]. However, a strong attachment of PMNCs on a hydrophobic surface needs at least 30% (molar ratio) of the catecholamine side chains. As some of the mussel mimetic universal adhesion catechol groups may appear on the surface and show their intrinsic adhesion with foulants, the exposed catechol groups need to be reacted or covered by designed materials, such as reactive phosphorylcholine copolymers, to reach better antifouling performance [37,38].

This current study aims to develop a simple and universal self-adhesion strategy for improving the antifouling performance of separation membranes with a new catecholic PC zwitterion copolymer (PMEND) coating by PDA mediated adhesion. A commercial polyethersulfone ultrafiltration membrane (PESUM) has been successfully coated for the first time to achieve such an objective (Scheme 1). The precoated PDA ultrathin layer on PESUM enhanced the adhesion and density of the catecholic phosphorylcholine copolymer. The optimized results showed that the immobilized PMEND film was stable in pH 3–10 water, air and gasoline for more than 2-weeks. More importantly, the water flux of this modified membrane could be recovered up to 100% and 93% after one and three cycles of protein fouling by 1.0 mg/mL BSA solution ultrafiltration, respectively. More interestingly, the modified membrane could remove 99.99% of oil contaminant from an 80,000 ppm oil/water emulsion.



Scheme 1. Illustrations of PESUM surface modification by PDA mediated PMEND coating and protein or oil rejection on the anchored cell membrane mimetic interface during ultrafiltration.

2. Experimental

2.1. Materials

Polyethersulfone ultrafiltration membrane (PESUM) with a diameter of 80 mm and molecular weight cut-off of 10 or 30 kDa was purchased from MoSu science equipment Company Limited (Shanghai, China). 3,4-dihydroxyphenethylamine (dopamine) hydrochloride and bovine serum albumin (BSA) were purchased from Sigma-Aldrich. 2-methacryloyloxyethyl phosphorylcholine (MPC) was purchased from Vertellus Specialties UK Ltd. *p*-nitro phenoxycarbonyloxyethyl methacrylate (NPCEMA) was synthesized according to a reported method [39]. Pure water (18.2 MΩ cm at 298 K) was prepared from a Millipore water purification system (Direct-Q3UV). All other chemicals and reagents were of analytical grade and were used without further purification unless otherwise indicated.

2.2. Synthesis of PMEN and PMEND

The structure and synthesis scheme of PMEN and PMEND random copolymers were shown in Fig. 1. PMEN was synthesized by a previously reported method with slight modification [36]. Briefly, predetermined amounts of NPCEMA and MPC were dissolved by ethanol in a 100 mL dropping funnel. AIBN (2 w% of the monomers) was dissolved in THF. One fourth of the AIBN solution was added into a 250 mL three necked flask containing 10 mL absolute ethanol heated to 70 °C. The remaining AIBN solution was mixed with the monomers and then added dropwise into the flask. The polymerization performed at 70 °C for 24 h under magnetic stirring and N_2 protection. The reacted solution was concentrated to one third in volume, and dialyzed in dialysis tubes (molecular weight cut-off of 7000 Da) against ethanol first and then phosphoric acid solution (pH 3.5). After freeze drying, the MPC and NPCEMA unit mole fractions of the PMEN copolymers were determined by ^{1}H NMR measurement with an Inova 400 Hz NMR spectrometer (Varian, USA).

The polymers bearing cell outer membrane PC, and mussel adhesive group dopamine (DA) side chains (PMENDs) were prepared by amidation of the active ester groups in PMEN with DA. The PMEN polymer was dissolved in ethanol and reacted with designed amount of DA at 60 °C for 12 h in nitrogen atmosphere. After adjusting the pH of the polymer solution to 3, the resulting PMEND was dialyzed in phosphoric acid solution (pH 3.5) and then lyophilized.

The molecular weights of the synthesized PMEN and PMEND polymers were characterized by a gel permeation chromatograph (GPC, Dionex Ultimate 3000) with a Shodex RI-101 refractive index detector and a Shodex OHpak SB-803 column. The system was calibrated with narrow molecular-weight poly (ethylene oxide) standards. The molar fractions of PC and DA side chain units in PMEND copolymers were determined by ^{1}H NMR measurement [38].

2.3. PDA coating

DA was dissolved in Tris/HCl buffer (pH=8.5) to form 2 mg/mL solution just before the coating experiment. The PESUM samples were immersed in the DA solution at room temperature for 1 h to form PDA coating. After washed thoroughly with pure water and ethyl alcohol, the PDA coated PESUM (PESUM/PDA) was dried in air at room temperature.

2.4. PMEND coating

PMEND polymer was dissolved in Tris/HCl buffer (pH=8.5) to form 4 mg/mL solution just before the coating experiment. The membrane samples of PESUM and PESUM/PDA were immersed separately in the PMEND solution for 24 h at room temperature. After washed thoroughly with pure water, PMEND coated PESUM