

Rapidly self-assembled polydopamine coating membranes with polyhexamethylene guanidine: Formation, characterization and antifouling evaluation



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HIGHLIGHTS

- A rapidly deposited PDA layer with PHMG was developed for hydrophilic modification.
- The PHMG had a significant impact on the dispersion and deposition of PDA coating.
- The diameter of PDA-PHMG capsules can be finely controlled at the nanometer scale.
- The modified membrane presented excellent permeation and antifouling performances.

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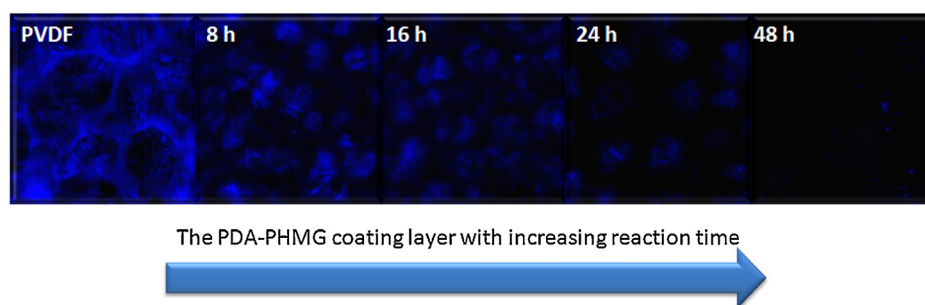
Polyhexamethylene guanidine

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GRAPHICAL ABSTRACT



ABSTRACT

A novel rapidly deposited polydopamine (PDA) layer with polyhexamethylene guanidine (PHMG) was developed for the modification of hydrophilic and antifouling poly(vinylidene fluoride) (PVDF) membranes on the basis of mussel-inspired surface chemistry in our latest work. The effect of PHMG on dopamine polymerization was investigated and experimental results demonstrated that the existence of water-soluble PHMG had a significant impact on the dispersion and deposition efficiency of PDA polymerized process due to strong interactions between PDA and PHMG. The morphology, structure, surface composition, and hydrophilicity of membranes were modified by the PDA-PHMG coating, as confirmed by scanning electron microscopy (SEM), confocal laser scanning microscope (CLSM), Fourier transform infrared spectroscopy (FTIR) and contact angle measurements. Acceleration of PDA polymerization was found to enhance the surface hydrophilicity and improve the water permeability of modified membranes. The PDA-PHMG coating membranes demonstrated excellent antifouling performances, including higher specific flux and flux recovery rate (FRR), lower adsorption of contaminants, and more resistant against irreversible fouling. The novel surface modification strategy was shown to be applicable to flat-sheet PVDF membranes and was relatively easy to operate under mild reaction conditions.

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1. Introduction

Membrane separation technology has been shown to be more effective compared with conventional wastewater treatment pro-

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cesses in terms of space requirements, effluent quality, reliability, and ease of operation [1]. However, high costs related to the regular replacement of membrane materials and maintenance to counteract membrane fouling can restrict the application of membrane technology [2]. Membrane fouling stems from interactions between the membrane material and components in the treated water, including precipitates from inorganic and organic matter, as well as microbial deposits [3,4]. Generally, fouling occurs when the constituents in the wastewater adsorb onto the membrane surface or deposit in membrane pores [2]. Numerous studies have shown that membrane fouling is a more serious concern with hydrophobic rather than hydrophilic materials due to hydrophobic interactions which occur among microbial cells, organic solutes, and the membrane interface [5]. Accordingly, several techniques, such as dip-coating [6], plasma treatment [7], surface grafting [8], and the addition of amphiphilic co-polymers [5,9], have been developed to hydrophilize or functionalize the membranes to reduce the potential for fouling. However, most of these techniques present one or more challenges, such as low stability of the coating or plasma surface, harsh operating conditions during grafting modifications, and high costs in combination with low market potential for further applications [10–12].

In 2007, Messersmith and co-workers reported a novel method to form multifunctional polymer coatings via polymerization of dopamine [13]. Their mussel-inspired polydopamine (PDA) coating has attracted considerable attention as a simple, robust, and universal technology to functionalize or hydrophilize the surface of materials. As a biomolecule containing catechol and primary amine functional groups, dopamine can be easily oxidized under alkaline conditions and spontaneously polymerizes to form a thin, hydrophilic, and tightly adherent PDA layer onto a wide range of inorganic and organic materials, including noble metals, oxides, polymers, semiconductors, and ceramics [11,13–16]. Due to the presence of large functional groups (e.g., carboxy, amino, imine, and phenol), the PDA can be dispersed in various solvents and displays excellent hydrophilicity [17,18]. Bourmaud et al. reported that the water contact angle can be reduced by more than 50° after 48 h of PDA polymerization [19]. For some special substrates, the contact angle after PDA coating can decrease drastically by over 90° to a final value near 20° [11]. Compared with traditional methods, the polymerization of dopamine is relatively simple and controllable and does not require any complicated instrumentation or harsh reaction conditions. The coating layer is also more stable over a relatively wide pH range (pH 1–10) [18]. Therefore, previous research studies have attempted to coat PDA layers to fabricate hydrophilic and antifouling membrane. Different types of membranes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes, have been modified by PDA coatings to enhance their fouling resistance to oil/water emulsions and protein mixtures [10,20–22]. Some hydrophobic polymer membranes or films, including polytetrafluoroethylene (PTFE), polyethyleneimine (PEI), poly(vinylidene fluoride) (PVDF), polyethersulfone (PES), and polyamide (PA), have been successfully hydrophilized by adhesive PDA coatings via dip-coating in aqueous dopamine solutions, resulting in a considerable improvement in antifouling properties [17,18,23–25]. However, the PDA deposition process usually requires more than 24 h to apply effective coating modifications [11]. In addition, the poor dispersion and lower deposition efficiency of PDA particles have reduced the effectiveness of this coating method.

The PDA concentration (thickness) on substrates surfaces can be controlled by changing the pH, monomer concentration, polymerization time, and oxidizing atmosphere. Nevertheless, increasing the concentration of the dopamine monomer or prolonging the reaction time has not been shown to effectively improve the deposition of PDA layer. As a result of abundant catechol groups, the

coatings on substrates surfaces may further conjugate other functional groups, such as –SH or –NH₂, via Michael addition and/or Schiff base reaction [10,11,26]. Thus, surfaces which have been modified by PDA could provide a useful platform for secondary reactions and surface functionalization for other modifiers, including poly(ethylene glycol) (PEG), Poly(N-vinyl pyrrolidone) (PVP) and other molecules containing –SH or –NH₂ [18,22]. In this work, we report a novel rapidly deposited PDA layer with polyhexamethylene guanidine (PHMG), a water-soluble polymer containing –NH₂ and –NH, where guanidine functional groups are connected by hexyl hydrocarbon chains [27]. The strong interactions between PDA and PHMG were studied for their ability to enhance deposition efficiency and improve the in-service performance of modified membrane by constructing a hydrophilic and antifouling surface. The improvement in PDA polymerization following reaction with PHMG and the effects of PDA-PHMG modification on hydrophilicity, water permeability, and antifouling properties of PVDF MF membranes were investigated. The surface composition and morphology of the modified membranes were also evaluated by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and confocal laser scanning microscope (CLSM). Overall, this method has demonstrated great potential of being a rapid and versatile approach for antifouling modification of porous membranes using polymerized PDA-PHMG coating.

2. Materials and methods

2.1. Materials

3, 4-Dihydroxyphenethylamine (dopamine hydrochloride) was obtained from J&K Scientific Ltd. and used as received. Polyhexamethylene guanidine hydrochloride (PHMG, 25%, FW = 211.16) was purchased from Nanjing Chemical Reagent Co., Ltd. Propidium iodide (DAPI) was obtained from Sigma-Aldrich. The flat-sheet PVDF membrane was supplied by Microdyn-Nadir Xiamen Co., Ltd, and nominal pore size of the membranes was 0.2 μm. Tris(hydroxymethyl)methyl aminomethane was procured from Sinopharm Chemical Reagent Co., Ltd., and dried yeast was purchased from Guangdong Danbaoli Instant Yeast Co., Ltd., which was washed thoroughly with water and then dispersed in de-ionized water using in membrane separation. The average yeast cell size was 5.9 ± 0.9 μm (range of 3.1–12.5 μm) determined by a Zetasizer Nano ZS (Malvern, UK). The de-ionized (DI) water was used in the sample preparation and for pure water flux measurements.

2.2. Surface modification of PVDF MF membranes

Pristine PVDF membranes were cut into circular pieces with a diameter of 70 mm, and soaked in ethanol for 1 h to remove the impurities adsorbed on the membrane surfaces. They were then dried to a constant weight in a vacuum oven at 40 °C. A 2.0 mg mL⁻¹ dopamine solution was prepared by dissolving 0.5 g of dopamine in 250 mL of Tris buffer solution (pH = 8.5, 50 mM) and 5.6 mL PHMG (with a mole ratio of 1:1 based on dopamine) was added to the dopamine solution. The pristine PVDF membranes were immediately immersed in the freshly prepared solution with continuous stirring at 25 °C under ambient conditions. After reacting for a designated time (8 h, 16 h, 24 h, 32 h, 48 h and 64 h), the modified PVDF membranes were taken out and washed three times with de-ionized water to remove free PDA or PHMG. The membranes were preserved in de-ionized water until further analysis. A second set of membranes was only immersed in a dopamine solution for 24 h without PHMG under identical conditions for comparison. The membranes are designated as PVDF, PDA coated and PDA-PHMG-

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