# A facile approach to fabrication of superhydrophilic ultrafiltration membranes with surface-tailored nanoparticles

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## ARTICLE INFO

## ABSTRACT

A hydrophilic membrane commonly performs better in resisting fouling. But most prevailing polymeric membrane materials are hydrophobic thus prone to be fouled in practical operations. The current study presents a facile strategy for the fabrication of superhydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes on the basis of a blending method and a dip-coating technique. A carboxyl-rich substance was firstly blended as an additive in the PVDF membrane matrix during fabrication. The incorporated carboxyl groups acted as anchor sites for the subsequent binding of amine-grafted silica nanoparticles (NPs). After a simple dip-coating operation, the PVDF membrane would be covalently functionalized to be superhydrophilic. Three types of carboxyl-rich additives including poly(methacrylic acid sodium salt), sodium alginate, and ethylenediaminetetraacetic acid (EDTA) were separately used to prepare different primary membranes for respective functionalization operations. The resultant membranes were systematically characterized in terms of hydrophilicity, morphology, permeability, and antifouling performance. Consequently, the simple dip-coating functionalization dramatically enhanced the surface hydrophilicity of all the additive-blended PVDF membranes. All the functionalized membranes obtained a significantly lower initial contact angle, which instantly reduced to < 5° within several seconds. This could be attributed to the hydrophilic chains grafted on the NPs and the proper micro-/nano-topography offered by the stack of NPs. Particularly, the EDTA-blended membranes achieved a higher and more stable hydrophilicity. Also, all the functionalized membranes obtained higher water permeabilities as compared with the pristine membrane. Moreover, all the superhydrophilic membranes restored over 80% flux (much higher than the ~53% for the pristine membrane) after cleaning in the fouling tests, demonstrating dramatically enhanced antifouling capacity.

## 1. Introduction

Wastewater reclamation is widely accepted as an efficient solution to the worldwide crisis of water scarcity [1,2]. Membrane separation technology, owing to its high treatment efficiency, small footprint, and good effluent quality, holds a dominant position in the wastewater reclamation market [3–5]. Micro-/ultra-filtration, as typical representatives of the low-pressure membrane separation processes, are commonly known as the most widely used membrane technology [6,7]. Compared with the high-pressure membrane technology (e.g., reverse osmosis [8] and nanofiltration [9]), the micro-/ultra-filtration processes effectively remove contaminants and pathogenic microorganisms from wastewater with less energy, satisfying the most radical purification demands [10,11]. This appropriate purification efficiency renders the micro-/ultra-filtration processes prominent in combating the increasing water scarcity.

The past decades have witnessed an astonishing growth of the engineering applications of the micro-/ultra-filtration processes in the field of wastewater treatment [3,5,12]. One of the most typical examples is membrane bioreactor [5]. However, as the admiration affection for its pleasing treatment quality fades away, the concern for its high operational cost due to membrane fouling is increasingly raised in the engineering field [6,13]. To achieve a sustainable development, the conquest of the long-standing membrane fouling problem becomes progressively urgent. On the basis of numerous studies in the past decades, the intrinsic hydrophobic property of the prevailing membrane materials (e.g., polyvinylidene fluoride, PVDF) has been widely recognized as one radical cause of membrane fouling [3,6,14–17]. Great efforts have been made to enhance the hydrophilicity of different membrane materials with various strategies including physical surface

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coating [18], physical blending [19,20], surface grafting [21,22], and so forth. The resultant hydrophilic membranes exhibited improved antifouling performance. However, there is definitely room to further increase the membrane hydrophilicity thus giving rise to superior fouling-resistant membranes. Superhydrophilic membranes which infinitely approach a maximized hydrophilicity can be expected to intrinsically solve the membrane fouling problem [6,15,23]. Fortunately, the prosperous development of nanomaterials and nanotechnology offered enormous opportunities for the fabrication of superhydrophilic membranes. Several nanomaterials, such as silica nanoparticles (NPs) [21,24], $TiO_2$ NPs [25,26], and tunicate cellulose nanocrystals [27], have been employed in constructing superhydrophilic surfaces. Whereas, relevant studies about the fabrication of superhydrophilic ultrafiltration membranes were rarely reported. Besides, the feasibility for commercial production was not sufficiently considered in the existing researches. It is imperative and beneficial to devote further efforts in this research field.

The present study proposed a facile strategy for the fabrication of superhydrophilic ultrafiltration membranes on the basis of our previous investigation [21]. A carboxyl-rich substance was firstly blended as an additive in the PVDF membrane matrix during fabrication. The incorporated carboxyl groups acted as anchor sites for the subsequent binding of amine-grafted silica NPs. After a simple dip-coating operation, the PVDF membrane could be covalently functionalized to be superhydrophilic. Poly(methacrylic acid sodium salt) (PMANa), sodium alginate (SA), and ethylenediaminetetraacetic acid (EDTA) were separately used as the carboxyl-rich substance. The resultant membranes were systematically characterized and compared. Filtration experiments with synthetic foulant solution demonstrated the conspicuous antifouling property of the functionalized membranes.

## 2. Materials and methods

### 2.1. Preparation of superhydrophilic NPs

Superhydrophilic NPs were prepared via silanization of silica NPs (Ludox HS-30, 30%, Sigma–Aldrich) as described previously [6,21]. Briefly, a 6 g portion of NPs was dispersed in 30 mL of DI water (Milli-Q ultrapure water purification system, Millipore, USA) under 30 min sonication (output power of 50 W, KQ5200E, Kunshan Ultrasonic Instruments, China). The obtained suspension was immediately mixed with 24 mL of freshly prepared silane solution comprising 87.5 g L$^{-1}$ of (3-aminopropyl)trimethoxysilane (97%, Sigma–Aldrich) under vigorous stirring. Afterwards, the mixture was adjusted to pH ~ 5 with 0.1 M HCl, followed by a 24 h stirring at 70 °C. Ultimately, the resultant suspension was dialyzed using SnakeSkin tubing (7 k MWCO, Pierce, USA) in deionized (DI) water and subsequently stored at 4 °C as stock NP suspension. A three-fold dilution was used for membrane functionalization.

### 2.2. Membrane fabrication and functionalization

Ultrafiltration membranes were fabricated via non-solvent induced phase separation [17]. Different casting solutions containing varied amounts of carboxyl-rich additives were prepared following the recipes in Table 1. To prepare the casting solution, 1 g of polyvinylpyrrolidone (PVP, average MW ~ 360,000, Sigma), 15 g of PVDF (average MW ~ 534,000, Aldrich), and a certain quantity of PMANa (MW ~ 483,000, Sigma–Aldrich), SA (Aldrich), or EDTA (≥99%, Fluka, USA) were vigorously dissolved in 84 g of N-Methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Sigma–Aldrich) at room temperature (23 ± 1 °C) for at least 8 h. Afterwards, a 12 h static storage (room temperature) and a 1 h heating operation (50 °C) were sequentially performed for bubble removal and annealing, respectively. To fabricate the membrane, the obtained casting solution was spread onto a glass plate at a thickness of 250 μm using a film applicator (Elcometer 3530,

Elcometer LTD., UK). After a 30 s exposure to air, the plate was immersed in a DI water bath, where polymer precipitation occurred thereby forming a membrane. After 12 min, the obtained membrane was detached from the glass plate and annealed in an 80 °C DI water bath for 5 min. After being thoroughly rinsed with DI water, the membrane was stored at 4 °C prior to use.

Membrane functionalization was accomplished via post-fabrication tethering of superhydrophilic silica NPs to the membrane surface through a facile dip-coating process. Firstly, the sample membrane was immersed in a catalytic solution comprising 2 mM N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (Thermo Scientific, USA), 5 mM N-hydroxysuccinimide (98%, Aldrich), and 10 mM 2-(N-morpholino)ethanesulfonic acid (as a buffer, 99%, J&K Scientific) at pH ~ 5 for 15 min. Secondly, the membrane was transferred to the superhydrophilic NP suspension and immersed for 12 h at pH 7–7.2. Finally, the functionalized membrane was rinsed with ample DI water and stored at 4 °C prior to characterization. The overall protocol for the fabrication of superhydrophilic membranes was illustrated in Fig. 1.

### 2.3. Membrane characterization

Membrane water permeability was tested with a dead-end filtration system, which contained a stirred cell (Amicon 8010, Millipore, USA), a constant pressure source (nitrogen), an electronic balance (ML4002, Mettler Toledo, USA), and a laptop for real-time data recording. The applied transmembrane pressure was determined according to the typical operational parameters employed in practical membrane-based processes for wastewater reclamation (e.g., membrane bioreactor) [5]. Prior to the test, the membrane specimen was pre-compacted in the stirred cell with DI water at 20 kPa for 20 min. Then the water flux was recorded at 10 kPa for 10 min. The water permeability ($J$, m s$^{-1}$ kPa$^{-1}$) was calculated as:

$$J = \frac{dV}{A\Delta P dt} \tag{1}$$

where the $V$, $A$, $\Delta P$, and $t$ indicate permeate volume, effective filtration area, transmembrane pressure, and filtration time, respectively. The final result for each membrane type (Table 1) was averaged from at least two measurements with separately fabricated membranes.

To characterize the physicochemical properties, the membrane sample was air-dried at room temperature. Membrane surface hydrophilicity was evaluated through water contact angle measurements using a video-supported optical instrument (OCA20, Dataphysics, Germany) on the basis of a sessile-drop method. A video displaying the variations of the shape profile of a 3 μL water droplet on the membrane surface was continuously recorded. The profile in each frame was fitted (SCA 20, Dataphysics, Germany) to calculate the contact angle. Both the static initial contact angle (when observable vibration of the water droplet just ceased) and dynamic decreasing trend of the calculated contact angles were employed to evaluate the hydrophilicity of the membrane surface. Additionally, the final static contact angle for each membrane was averaged from over seven measurements at different locations.

The irreversibility of NP binding on the functionalized membrane was assessed with both physical and chemical stress tests. The physical stress was implemented by twice 1 min sonication (50 W) in a DI water bath. The chemical stress was separately applied by a 15 min immersion in a pH 2 HCl solution, a pH 12 NaOH solution, or a 5 M NaCl solution, followed by an adequate rinse with DI water. Afterwards, contact angle measurements in both the static and dynamic manners were performed to evaluate the changes of membrane surface hydrophilicity.

Functional groups of the membrane surfaces were characterized with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, VERTEX 70, Bruker, Germany). Membrane morphology was observed with a field emission scanning electron microscope (FE-SEM, SU8010, Hitachi, Japan). The cross-sectional samples