



Multiple antifouling capacities of hybrid membranes derived from multifunctional titania nanoparticles



Xueting Zhao^{a,b}, Yanlei Su^{a,b}, Yanan Liu^{a,b}, Runnan Zhang^{a,b}, Zhongyi Jiang^{a,b,*}

^a Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, No. 92, Weijin Road, Nankai District, Tianjin 300072, China

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

ARTICLE INFO

Article history:

Received 16 June 2015

Received in revised form

10 August 2015

Accepted 11 August 2015

Available online 14 August 2015

Keywords:

Hybrid membranes

Multifunctional inorganic nanoparticles

Surface heterogeneity

Hierarchical topographies

Multiple anti-oil-fouling mechanisms

ABSTRACT

Hybridization has evolved a powerful toolbox for hierarchical structure manipulation of antifouling membrane surface. In this study, zwitterionic and fluorine-containing moieties are immobilized onto the surface of TiO₂ nanoparticles through the mediation of polydopamine, and the resultant nanoparticles are incorporated into poly(vinylidene fluoride) (PVDF) matrix to simultaneously manipulate the chemical and topological structures of membrane surfaces. The hierarchical topographies of the hybrid membranes arise from the morphology of nanoparticles. The surface heterogeneity of the hybrid membranes arises from the different chemical moieties on nanoparticles, endowing the membrane surfaces with both hydrophilic zwitterionic segments and low surface energy fluorine-containing segments. Due to the favorable hierarchical chemical and physical structures, the hybrid membranes display a remarkable enhancement in oil-fouling-resistant and oil-fouling-release capacities during oil-in-water emulsion filtration: the flux declines at the minimum level of 16.7% and recovers to the maximum level about 100%. It can be anticipated that the present study will offer a physico-chemical coordinated antifouling mechanisms to control membrane oil-fouling for the efficient oil-containing wastewater treatment.

© 2015 Elsevier B.V. All rights reserved.

1 Introduction

Global water crisis poses growing challenge to sustainable development, especially for developing countries. For the last five years, the total volume of wastewater discharge in China is calculated as more than 60 billion ton/year, which far exceeds environmental capacity. Membrane technology is regarded as the most efficient approach for advanced wastewater treatment and reuse in refinery and petrochemical industries. However, most of membranes suffer from inevitable fouling in the implementation [1–3]. Membrane fouling is caused by complicated interactions (hydrogen-bond, electrostatic, hydrophobic, etc. [4–6]) between foulants and membranes, resulting in extra cost and energy requirements. For effective wastewater treatment, antifouling membranes that are capable of preventing or minimizing the direct interactions between foulants and membranes are becoming imperative requirement.

The rational design of high-performance antifouling membranes

* Corresponding author at: Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, No. 92, Weijin Road, Nankai District, Tianjin 300072, China. Fax: +86 22 27406646.

E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

relies heavily on the innovation in reliable fabrication methods and efficient antifouling mechanisms. To date, hybridization approach has attracted remarkable attention for the construction of antifouling membrane surfaces. For example, hydrophilic inorganic nanoparticles (NPs) and carbon-based nanomaterials have been incorporated in membrane modification to improve surface hydrophilicity and antifouling capacities [7–11]. More importantly, inorganic nanomaterials have also been used as robust carriers to immobilize a variety of antifouling moieties on membrane surfaces. Neutral and hydrophilic brushes, such as poly(2-hydroxyethyl methacrylate) [12–14], poly(ethylene glycol) [15,16], poly(zwitterionic methacrylate) [17–20], poly(1-vinylpyrrolidone) [21] and polyamines [22,23], have been grafted on inorganic nanomaterials and successfully anchored on the surfaces of hybrid membranes. These hydrophilic brushes facilitate the surface hydration of hybrid membranes via hydrogen-bond or electrostatic interactions, which endows hybrid membranes with outstanding antifouling performance.

The efficient antifouling mechanisms are considered as the critical issues for the construction of antifouling membranes. In general, antifouling mechanisms have been catalogued as fouling-resistant mechanism and fouling-release mechanism. The core of fouling-resistant mechanism is to generate compact hydration layer barrier and robust steric repulsion effects between foulants and surfaces so that the attachment of foulants onto hydrophilic

surfaces can be prevented [24,25]. The core of fouling-release mechanism is to weaken or minimize the interfacial polar or hydrogen bonding interactions between foulants and low surface energy surfaces so that the attached foulants can be more readily removed by hydraulic shear forces [26–28]. Recently, the pursuit of robust antifouling capacities triggers the transformation of antifouling mechanisms from single mode to multiple mode. Pioneering works of Wooley et al. [29,30] and Ober et al. [31] reported the superior antifouling capacities of marine coating with surface heterogeneity by coordinating the fouling-resistant mechanism of poly(ethylene glycol) chains and the fouling-release mechanism of fluorinated chains. Advances in antifouling polymeric membranes with tunable fouling-release and fouling-resistant attributes contribute to increased flux recovery and decreased flux decline during membrane filtration [32–35]. However, the effective routes to engineer the multiple antifouling mechanisms of membranes are still limited. Thanks to the multiple functionalities and multi-scale structures of hybrid membranes, it can be envisioned that hybridization manipulation strategy can provide a competitive approach to confer multiple antifouling capacities to membranes for enhanced separation performance.

Oil is usually considered as one of the major foulants in membrane processes for industrial oil-containing wastewater treatment. The low surface tension of oil foulants makes oil-fouling more complicated. Although previously reported hybrid membranes have shown superior anti-oil-fouling capacities by co-constructing the oil-fouling-resistant mechanism of TiO_2 NPs and the oil-fouling-release mechanism of fluorinated group [36,37], the topological structure was rarely taken into account. Consequently, the synergistic effects of surface chemical and topological structures on the anti-oil-fouling capacities of hybrid membranes are essential and should also be investigated more extensively. In this study, polydopamine-coated TiO_2 NPs (TiO_2 @PDA NPs) are synthesized by one-step deposition and self-polymerization of dopamine, which serve as the carrier to anchor both zwitterionic and fluorine-containing antifouling moieties. The modified TiO_2 @PDA NPs are incorporated into PVDF membrane matrix to endow membrane surfaces with both surface heterogeneity and hierarchical topographies. The topographies of membranes are evaluated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The heterogeneity of the membranes are assessed by X-ray photoelectron spectroscopy (XPS), contact angle measurement and surface energy analysis. The synergistic effects of surface heterogeneity and nano-structured surface topology on the anti-oil-fouling property of membranes during oil-in-water emulsion filtration have been investigated and discussed in detail.

2 Experimental

2.1 Materials

Poly(vinylidene fluoride) (PVDF, FR-904) was obtained from Shanghai 3F New Material Co. Ltd. and dried at 110 °C for at least 12 h before use. 2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFBM) was supplied by Xeogia Fluorine-Silicon Chemical Co. Ltd. and washed twice with a sodium hydroxide solution (1 mol/L) and deionized water to remove the inhibitor before use. [2-(Methacryloyl)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide inner salt (SBMA) and tris(hydroxymethyl) aminomethane (Tris) were purchased from Sigma-Aldrich Co. N-vinylformamide (NVF) was purchased from Tokyo Chemical Industry Co. Ltd. 2,2'-Azobis (2-methylpropion-amidine) dihydrochloride (AIBA) was purchased from J&K Scientific Ltd. Dopamine hydrochloride (DA) was purchased from Yuancheng Technology Development Co. Ltd. Titanium dioxide nanoparticles (TiO_2 NPs) was purchased from

Aladdin Industrial Inc. High-speed vacuum pump oil (GS-1) was purchased from Beijing Sifang Special Oil Factory. Polyethylene glycols (PEG), N-methyl-2-pyrrolidone (NMP), sodium dodecylsulfate (SDS) and other chemicals were obtained from Tianjin Guangfu Fine Chemical Research Institute.

2.2 Synthesis of zwitterionic and fluoride-containing modifiers

$\text{H}_2\text{N-PVNF-Z}$ and $\text{H}_2\text{N-PVNF-F}$ copolymers were synthesized via AIBA initiated free radical polymerization in aqueous solution followed by acidic hydrolysis. The synthetic procedure was shown in Fig. S1. NVF (20 mmol) was added into water (50 ml) and purged with N_2 for 30 min to remove oxygen. AIBA (0.5 mmol) was dissolved in water (6 ml) and added into the NVF solution. The polymerization was carried out at 52 °C for 2 h under nitrogen atmosphere. After 2 h, the SBMA (Z) aqueous solution (1.43 mol/L, 14 ml) or SDS-stabilized HFBM (F) emulsion (1.43 mol/L, 14 ml) were added dropwise into the above solution. Polymerization was performed at 52 °C for another 8 h under nitrogen atmosphere and then terminated by cooling and exposing to air. After polymerization, hydrochloric acid (37 wt%, 7 ml) was added into the solution of PVNF-Z or PVNF-F copolymer and hydrolysis was performed at 70 °C for 2 h to convert amide group into amine group. The resultant polymer solution was dialyzed in dialysis tubing (molecular weight cut-off, 3500 Da) against water for at least 72 h and then dried under vacuum. The obtained $\text{H}_2\text{N-PVNF-Z}$ and $\text{H}_2\text{N-PVNF-F}$ copolymers were characterized by Nicolet 6700 Fourier transform infrared (FTIR) spectrometry and INVOA-500 ^1H nuclear magnetic resonance (^1H NMR) spectrometer (see the Supporting information).

2.3 Preparation of TiO_2 @PDA NPs and modified TiO_2 @PDA NPs

TiO_2 NPs (1.0 g) and PEG 400 (50 mg) were pre-dispersed in Tris-HCl buffer (50 mM, pH=8.5, 100 ml) and sonicated for 30 min for uniform dispersion. Then, the dispersion was subjected to high-speed stirring and DA (200 mg) was added. After oxidant-induced surface polymerization of DA for 24 h at 30 °C, the as-prepared TiO_2 @PDA NPs were collected and washed by centrifugation. To prepare modified TiO_2 @PDA NPs with different functional segments, the obtained TiO_2 @PDA NPs were dispersed in Tris-HCl buffer (50 mM, pH=8.5, 45 ml) by sonicator, followed by mixing with the aqueous solution of $\text{H}_2\text{N-PVNF-Z}$ (100 mg/ml, 5 ml), $\text{H}_2\text{N-PVNF-F}$ (100 mg/ml, 5 ml) or both. The mixture was subjected to high-speed stirring at 60 °C for 2 h. The $\text{H}_2\text{N-PVNF-Z}$ and $\text{H}_2\text{N-PVNF-F}$ copolymers could be covalent linked with the PDA shell on TiO_2 NPs by primary amine groups. The as-prepared TiO_2 @PDA-Z, TiO_2 @PDA-F and TiO_2 @PDA-ZF NPs were collected and washed by centrifugation. Fig. 1 presents a schematic diagram of PDA-based modification procedure. The obtained TiO_2 @PDA NPs and modified TiO_2 @PDA NPs were characterized by Nicolet 6700 FTIR spectrometry, NETZSCH TG209 F3 thermogravimetric analysis (TGA, air atmosphere), Nanosem 430 energy dispersive X-ray spectroscopy (EDS) and JEM-2100F transmission electron microscopy (TEM).

2.4 Fabrication of hybrid membranes

Hybrid membranes derived from TiO_2 @PDA NPs and modified TiO_2 @PDA NPs were fabricated by non-solvent induced phase inversion (NIPS). The TiO_2 @PDA NPs or modified TiO_2 @PDA NPs (20 wt% versus the weight of PVDF) were added to the NMP sonicated for 30 min for uniform dispersion. Then, PVDF (12 wt%) and PEG2000 (6%) were added to the dispersions and stirred for 12 h at 60 °C to form homogeneous casting solutions. After degassing for 12 h, the casting solutions were cast onto glass plates

Download English Version:

<https://daneshyari.com/en/article/632712>

Download Persian Version:

<https://daneshyari.com/article/632712>

[Daneshyari.com](https://daneshyari.com)