



Comparison of antifouling behaviours of modified PVDF membranes by TiO₂ sols with different nanoparticle size: Implications of casting solution stability

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ABSTRACT

Widespread applications of membrane technology call for the development of antifouling membranes, and preparation of mixed matrix membranes (MMMs) by mixing nanoparticles (NPs) into polymeric membrane matrix has attracted much attention. In this work, polyvinylidene fluoride (PVDF) MMMs were prepared by two TiO₂ sols with different NPs size (one from hydrolysis and condensation with an average size of 5 nm, and the other from dispersion of TiO₂ nanoparticles with a particle size of 21 nm), and comparison of their antifouling behaviours was conducted. Compared to the pristine PVDF membrane (N0) and membrane (N1) modified by TiO₂ sol from dispersion of TiO₂ NPs, the surface pore size, porosity and permeability of modified membrane (N2) by TiO₂ sol from hydrolysis and condensation were slightly decreased, while the hydrophilicity and the absolute value of Zeta potential were obviously improved. Moreover, the N2 membrane showed a higher surface energy barrier, smaller frequency shift in quartz crystal microbalance with dissipation monitoring, and higher relative flux than N1, indicating a better antifouling performance. The abundant hydroxyl groups and the increased Ti and O elements on the membrane surface accounted for the enhanced hydrophilicity and antifouling ability. Scanning electron microscope (SEM) images clearly show that TiO₂ particles were uniformly distributed for N2; however, the severe agglomeration and sedimentation were observed for N1. Multiple light scattering spectroscopy (MLiSSP) analysis showed that N2 casting solution had a higher stability as revealed by the negligible backscattering change, decreased demixing thickness and low turbiscan stability index (TSI) value. The different stability of casting solutions might result in the different NPs' behaviours during membrane formation process, accounting for the discrepancy in the physicochemical properties and antifouling ability between N1 and N2 membranes.

1. Introduction

Recently, TiO₂ nanoparticles (NPs) have received much attention for being used as functional additives to improve physicochemical properties of polymeric membranes because of their excellent stability, non-toxicity, and good affinity to water [1–3]. Different methods including coating, blending, and deposition can be used to prepare NPs/organic polymer mixed matrix membranes (MMMs) [4]. Among them, blending nano-TiO₂ NPs directly into polymeric membrane casting solutions is considered as a simple and effective method to fabricate MMMs [5].

Current blending strategies for preparing MMMs involve the blending of TiO₂ sol from dispersion of nanoparticle powders (Sol-D) [6–8] and the use of nano-TiO₂ sol from hydrolysis and condensation

of titanium alkoxide (Sol-HC) [9,10]. Due to the high surface energy nature of nano-TiO₂, the agglomeration of nano-TiO₂ has been reported to occur in the MMMs using Sol-D, which significantly inhibits the modification efficiency and even deteriorates membrane intrinsic properties [6–8]. The use of TiO₂ Sol-HC, inducing the hydrolysis and polycondensation reactions to form NPs in polymer matrix during membrane fabrication, might restrain the agglomeration phenomenon [11–13], although the underlying mechanism is not very clear. There is also an obvious lack of detailed comparison of MMMs modified by these two sols for elucidating their different modification effects.

The modification efficiency relies heavily on the dispersion of TiO₂ NPs in the matrix, which may be closely related to the existing status of NPs in the casting solutions. This enables us to put forward a

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hypothesis that the casting solution stability might correlate with the physicochemical properties of MMMs. In fact, solution stability has been reported to significantly affect the oil/water demulsification, flocculation efficiency and particle sedimentation in mixed liquors [14–16]. Inspired by these studies in water chemistry, we investigated the stability of membrane casting solutions using multiple light scattering spectroscopy (MLiSSP) and attempted to explain the differences in physicochemical properties of the MMMs using these two TiO₂ sols (i.e., Sol-D and Sol-HC).

The objective of the present work was therefore: (i) to compare the antifouling properties of MMMs modified by Sol-D from dispersion of nanoparticle powders and Sol-HC from hydrolysis and condensation of titanium alkoxide, in which the classical extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory and quartz crystal microbalance with dissipation monitoring (QCM-D) were used to evaluate and monitor their fouling behaviours, and (ii) to discuss the implications of casting solution stability for the physicochemical properties of MMMs by using MLiSSP. In this work, the polyvinylidene fluoride (PVDF) polymeric matrix was used since PVDF is a widely-used membrane material because of its excellent chemical resistance, high mechanical strength and thermal stability [5,7,8].

2. Materials and methods

2.1. Reagents

Commercial grade PVDF (Solef® 6020, Mw=670–700 kDa) was obtained from Solvay Corporation. Dimethylacetamide (DMAC) and dimethylsulfoxide (DMSO) used as solvents, polyethylene glycol (PEG 400) used as a pore-forming additive, tetrabutyl titanate (Ti(OBu)₄, 98%), nitric acid (HNO₃, 65%), and ethyl alcohol (EtOH, 99.5%) were supplied by Sinopharm (Shanghai, China). Sodium hypochlorite (NaClO, with 10–15% of available chlorine) and bovine serum albumin (BSA, 67 kDa) were purchased from Sigma-aldrich. The phosphate buffered saline (PBS, pH=7.4) was obtained by dissolving buffer salts (0.790% NaCl, 0.020% KCl, 0.142% Na₂HPO₄ and 0.024% KH₂PO₄) in deionized (DI) water. 1 g/L BSA with PBS solution at pH 7.0 adjusted by 0.1 M NaOH or 0.1 M HCl was used as a model foulant in this study.

2.2. Preparation of TiO₂ sol solutions with different primary particle size of titania

TiO₂ Sol-D in this study was prepared by dispersing TiO₂ nanoparticles powder (purchased from Sigma-aldrich) in the mixed solvents under ultrasonic treatment for 30 min, with an average particle size of

Table 1

Detailed chemical compositions of membranes N0–N2 (unit: wt%).

Membranes	PVDF	Solvent (DMAC and DMSO)	PEG	TiO ₂
N0	10	80	10	0
N1	10	80	10	0.25
N2	10	80	10	0.25

21 nm (Fig. 1). TiO₂ Sol-HC was prepared from the hydrolysis and condensation of titanium alkoxide, and the preparation process was described as below. Ti(OBu)₄ (8.6 mL), used as a precursor, was added to 17.7 mL EtOH under magnetic stirring at a speed of 1000 rpm for 30 min. Another 8.9 mL EtOH, 3.6 mL DI water and 1.8 mL HNO₃ were mixed and stirred for 30 min. The EtOH/DI water/ HNO₃ solution was dropwise added to the Ti(OBu)₄ solution with vigorous stirring for 2 h at room temperature, obtaining the stable and homodispersed TiO₂ sol. The transmission electron microscopy images of two kinds of suspensions, namely TiO₂ Sol-D and TiO₂ Sol-HC can be found in Fig. 1.

2.3. Membrane preparation

Membranes used in this study were prepared by a phase inversion method via immersion precipitation. The detailed chemical compositions for membrane preparation are shown in Table 1. Briefly, a predetermined amount of PVDF and PEG was dissolved in a solvent mixture comprised of 50 vol% DMAC and 50 vol% DMSO. The suspension was agitated at 80 °C for 5 d to obtain a homogeneous solution. In the meantime, two TiO₂ sols were prepared by either dispersing a preweighted amount of TiO₂ sol made from hydrolysis and condensation of titanium alkoxide (0.25 wt%) or TiO₂ NPs powder (0.25 wt%) in a DMAC/DMSO solvent mixture. Subsequently, the two solutions were mixed and stirred at 80 °C for 2 d to obtain the casting solution. Finally, the dope solution was casted on porous polyester non-woven fabrics with a casting knife gap of 250 μm. The casted films were allowed to evaporate for approximately 20 s before immersed into a coagulation bath of deionized water at room temperature. The resulting membranes were denoted as N1 (TiO₂ Sol-D) and N2 (TiO₂ Sol-HC), respectively, while the pristine PVDF membrane without TiO₂ (named as N0) was used as a control.

2.4. Membrane characterization

Membrane morphologies of the surfaces and cross sections were

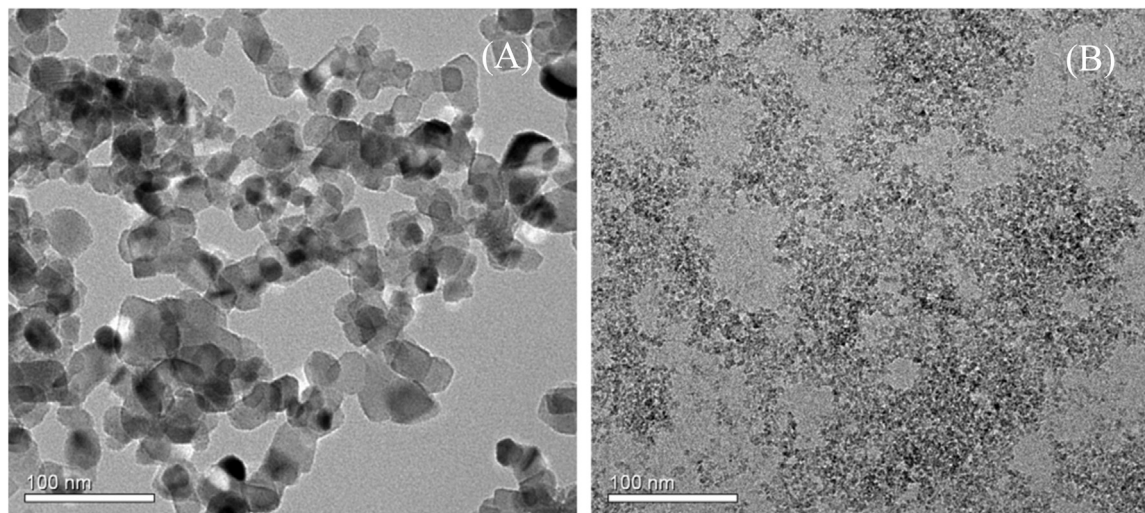


Fig. 1. TEM images of (A) TiO₂ sol (Sol-D) from dispersion of TiO₂ NPs (21 nm) and (B) TiO₂ sol (Sol-HC) from the hydrolysis and condensation of titanium alkoxide (5 nm).

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