



Surface zwitterionization of poly(vinylidene fluoride) membranes from the entrapped reactive core–shell silica nanoparticles

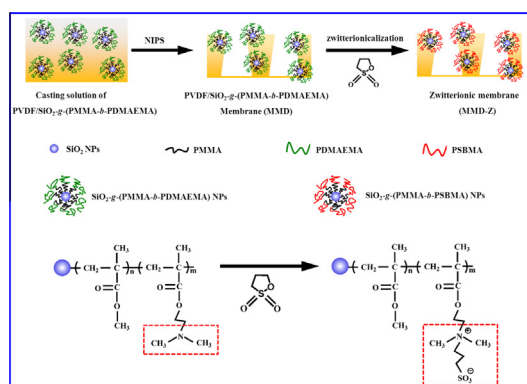


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GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate the preparation and properties of poly(vinylidene fluoride) (PVDF) filtration membranes modified via surface zwitterionization mediated by reactive core–shell silica nanoparticles (SiO₂ NPs). The organic/inorganic hybrid SiO₂ NPs grafted with poly(methyl methacrylate)-*block*-poly(2-dimethylaminoethyl methacrylate) copolymer (PMMA-*b*-PDMAEMA) shell were prepared by surface-initiated reversible addition fragmentation chain transfer (SI-RAFT) polymerization and then used as a membrane-making additive of PVDF membranes. The PDMAEMA exposed on membrane surface and pore walls were quaternized into zwitterionic poly(sulfobetaine methacrylate) (PSBMA) using 1,3-propane sultone (1,3-PS) as the quaternization agent. The membrane surface chemistry and morphology were analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. The hydrophilicity, permeability and antifouling ability of the investigated membranes were evaluated in detail. It was found that the PSBMA chains brought highly-hydrophilic and strong fouling resistant characteristics to PVDF membranes due to the powerful hydration of zwitterionic surface. The SiO₂ cores and PMMA chains in the hybrid NPs play a role of anchors for the linking of PSBMA chains to membrane surface. Compared to the traditional strategies for membrane hydrophilic modification, the developed method in this work combined the advantages of both blending and surface reaction.

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1. Introduction

In order to overcome the scarcity of portable water, membrane separation (microfiltration, ultrafiltration, nanofiltration, reverse osmosis, membrane distillation and so on) has been widely applied in water treatments such as seawater desalination and wastewater purification [1,2]. The heart of the membrane-based water treatment processes is the membrane, which can remove hazardous materials such as microorganisms, biological metabolites and excess metallic salts from water samples. Separation membranes are mainly made of synthetic polymer materials such as polyvinylidene fluoride (PVDF), polyethersulfone (PES) and polysulfone (PSF) [3–5]. PVDF is one of the most favorable membrane materials to fabricate ultrafiltration and microfiltration membranes due to its excellent mechanical strength, chemical resistance, thermal stability, etc. [6,7]. However, the future of PVDF membrane is suppressed to some extent due to its intrinsic hydrophobic nature. In the case of hydrophobic PVDF membranes, pollutants (such as proteins and colloids) in water are easily adsorbed and deposited onto the membrane surfaces and pores via hydrophobic interaction, causing membrane fouling as well as the deterioration of membrane permeability and service life [8].

Hydrophobic interaction between foulants and membrane surface is the main factor for the formation of membrane fouling. Therefore, hydrophilic modification of the hydrophobic membrane materials is a commonly used strategy to reduce the fouling trend of polymer membranes during aqueous separation process [9–11]. Numerous methods have been reported on the modification of PVDF membranes to improve their hydrophilicity and antifouling ability, which can be mainly divided into bulk modification [12] (raw material modification and blending) and surface modification [13,14] (surface grafting, interfacial polymerization, etc.). Compared to other methods, blending modification is a more preferable method to be applied for industrial-scale production. Poly(ethylene glycol) (PEG), poly(*N*-vinyl pyrrolidone) (PVP), poly(methyl methacrylate) (PMMA) and amphiphilic copolymers are the most popular additives. Apart from polymeric additives, various inorganic nanomaterials including nanoparticles [15–17], carbon nanotubes [18,19] and grapheme oxides [20–22] are popularly blended with PVDF to fabricate hybrid membranes. It is reported that the obtained hybrid membranes often exhibit higher thermal and chemical stability than that of pure polymer membranes. Furthermore, it has been found in some studies that both water flux and rejection of the hybrid membranes were significantly improved [23,24]. The results indicate that the trade-off between the permeability and selectivity of polymer membranes has been overcome.

SiO₂ nanoparticles (SiO₂ NPs) have been proved to be one of the most favorable inorganic nanomaterials used as additives due to its low cost, good size controllability and surface reactivity [25–28]. Also they can be conveniently synthesized in laboratory via classical Stöber sol–gel method [29]. However, pure inorganic nanomaterials will easily aggregate in polymer matrix due to their high specific surface area and reactivity, leading to the formation of big defects and a decrease in membrane selectivity. Therefore, it is necessary to modify the surface of nanomaterials to improve their dispersity and miscibility in the polymer matrix. One of the most interesting approaches to modify the inorganic nanomaterials is to graft polymer to/from the surface of inorganic materials via reversible addition fragmentation chain transfer (RAFT) polymerization, atom transfer radical polymerization (ATRP) and so on [30–34].

In our previous work, poly(2-hydroxyethyl methacrylate) (PHEMA) grafted silica nanoparticles (SiO₂-g-PHEMA NPs) and poly(2-dimethylaminoethyl methacrylate) grafted silica nanoparticles (SiO₂-g-PDMAEMA NPs) have been synthesized via RAFT polymerization, and they were used as additive to modify PES

membranes, respectively [24,35]. We found that the hybrid nanoparticles could be better dispersed and held in/on the PES membrane for a long period of time than that of pure SiO₂ NPs. More importantly, the trade-off between permeability and selectivity of PES membranes was overcome by the incorporation of each hybrid nanoparticles. Furthermore, PDMAEMA chains enriched on the surfaces and pore walls of the prepared PES/SiO₂-g-PDMAEMA membranes were further transformed into polyzwitterions and polycations by quaternization. The obtained zwitterionic and cationic PES membranes exhibited excellent anti-fouling and antibacterial activities, respectively. Compared with PHEMA and PDMAEMA, it has been reported that poly(methyl methacrylate) (PMMA) provides perfect compatibility with the PVDF matrix [36–38]. In order to enhance the stability and hydrophilicity of the modified PVDF membranes, PMMA based amphiphilic copolymers are the most competitive additives since Mayes et al. preliminarily reported the protein resistant PVDF membrane using the amphiphilic comb-like copolymer P(MMA-*r*-POEM) as additives in 1999 [39]. The relatively hydrophobic PMMA provides compatibility with PVDF and water insolubility during filtration process, while hydrophilic chains deliver fouling resistance. However, rare work has been reported on the modification of PVDF membranes using PMMA based amphiphilic copolymer grafted SiO₂ NPs as additives.

In this work, PMMA-*b*-PDMAEMA grafted silica nanoparticles (SiO₂-g-(PMMA-*b*-PDMAEMA) NPs) were prepared via surface-initiated RAFT polymerization and they were applied as additive to prepare PVDF/SiO₂-g-(PMMA-*b*-PDMAEMA) hybrid microporous membranes via non-solvent induced phase separation (NIPS) process. PMMA chains grafted on SiO₂ NPs can restrain the aggregation of SiO₂ NPs in PVDF matrix and improve the miscibility between organic phase and inorganic phase in hybrid membrane. Furthermore, PDMAEMA chains can be transformed into polyzwitterions by quaternization with 1,3-propane sultone (1,3-PS). The morphology, chemistry performances of the hybrid membranes before and after surface zwitterionization were investigated in detail.

2. Materials and methods

2.1. Materials and reagents

Poly(vinylidene fluoride) (PVDF 1015, $M_n = 2.1 \times 10^5$ g mol⁻¹) was supplied by Solvay Company. 1,3-propane sultone (1,3-PS), tetraethyl orthosilicate (TEOS), (3-aminopropyl)triethoxysilane (APTES), 4,6-dimethyl-2-pyridinamine (DMAP) and *N,N'*-dicyclohexylcarbodiimide (DCC) were provided by Aladdin and used directly. Methyl methacrylate (MMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) were bought from Aladdin and passed through a column filled with basic alumina to remove the polymerization inhibitor. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemical Regent Company and recrystallized from ethanol. Bovine serum albumin (BSA) was supplied by Bio Life Science and Technology Co. (Shanghai, PR China). 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid (CDP) was synthesized according to the method in the literature [40]. All other reagents, such as *N,N*-dimethylacetamide (DMAc) and ethanol were in analytical grade and used without further purification. Ultrapure water was produced by a Millipore direct-Q system and used throughout the experiments.

2.2. Synthesis of SiO₂-g-(PMMA-*b*-PDMAEMA) NPs via SI-RAFT polymerization

The SiO₂-g-(PMMA-*b*-PDMAEMA) NPs were prepared by serially grafting PMMA and PDMAEMA brushes onto SiO₂ NPs via SI-RAFT

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