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# A green approach to porous and dense antifouling membranes through solvent-free bulk polymerization



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## HIGHLIGHTS

- A solvent-free approach to fabricate dense and porous membranes was developed.
- The membrane pores can be controlled by the size of silica nanoparticles.
- The membranes exhibited high antifouling and separation performance.

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## ABSTRACT

In this study, a green approach to prepare both porous and dense antifouling membranes was developed through solvent-free bulk polymerization of the casting solution containing 2-hydroxyethyl methacrylate (HEMA) and pre-dispersed silica nanoparticles in two glass sheets under pressure. Porous polyHEMA membranes were prepared *via* removing the silica nanoparticles embedded in the polymer matrix. Dense poly(HEMA/MAA)/SiO<sub>2</sub> membranes were fabricated by adding methacrylic acid (MAA) as co-monomer without removing the silica nanoparticles. Membrane thickness could be conveniently controlled by varying the distance between the two slide glasses. Field emission scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and water contact angle measurement were employed to characterize the morphology and surface chemical composition of the resultant membranes. The porous polyHEMA membranes exhibited high efficiency in purification of bovine serum albumin (BSA) from BSA/yeast solution while the dense poly(HEMA/MAA)/SiO<sub>2</sub> membranes exhibited high rejection of orange GII. Both porous membranes and dense membranes exhibited strong hydrophilicity as a result of hydrophilic monomer HEMA, leading to good antifouling properties.

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## 1. Introduction

As a green and efficient technology, membrane separation technology has been broadly applied in wastewater treatment, bio-separation as well as food and pharmacy industries (Shannon et al., 2008; Blöcher et al., 2003). At present, a majority of membranes are prepared by organic solvent based approaches, such as phase inversion approaches for porous membranes and interfacial polymerization approaches for dense membranes. In phase inversion approaches, organic solvents such as N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP),

dissolve the bulk polymer and some additive(s) to make viscous homogeneous casting solutions (Zhao et al., 2008; Tian and Jiang, 2008; Liu et al., 2012; Xu and Qusay, 2004). The exchange between the organic solvent and the nonsolvent (usually water) causes a liquid–liquid phase separation, followed by the precipitation of the dissolved bulk polymers to acquire solid membranes. In interfacial polymerization approaches, organic solvents, such as n-hexane and n-heptane, play an essential role of dissolving the organic monomer and creating the interface with water for the rapid reaction between two reactive monomers (Mansourpanah et al., 2009; Lee et al., 2011).

However, as we know, organic solvents are usually harmful to both human body and natural environment. Organic solvents used in membrane fabrication are often toxic to the nervous system, respiratory system, liver and kidney, and may induce chronic skin diseases (Houck et al., 1992; Schenker and Jacobs, 1996; Yang et al., 2000). For instance, DMAc is repellent for damaging liver and causing toxic

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hepatitis, while DMF is even suspected to be associated with cancers and chromosomal aberration (Baum and Suruda, 1997; Choi et al., 2001; Cai et al., 1992; Midorikawa et al., 2000; Zhang et al., 2010). As typical volatile organic compounds (VOCs), n-hexane and n-heptane are toxic for humans and animals above certain doses (Guo et al., 2009; Muezzinoglu et al., 2001). Moreover, it is difficult to dispose or recycle organic solvents in membrane manufacturing wastewater due to their stability, high boiling points and low concentrations. It can be conjectured that an environmentally friendly approach for both porous and dense membrane preparation will be desired for the sustainable development of membrane science and technology.

In our recent study, a solvent-free approach to porous antifouling membranes was developed tentatively (Peng et al., 2013). 2-hydroxyethyl methacrylate (HEMA) was used as a liquid monomer, which dissolved other additives and formed the membrane matrix through bulk polymerization. Tetraethyl orthosilicate (TEOS), as a pore-forming agent, generated silica nanoparticles *via* sol–gel process, which were further removed, leading to the membrane pores. However, the membrane pore size could not be controlled because the free radical polymerization, which was rather fast, constrained the size of the TEOS aggregates. In this study, we further explored this solvent-free approach by preparing both porous and dense antifouling membranes *via* bulk polymerization and solidification of 2-hydroxyethyl methacrylate (HEMA) without organic solvents. The big difference from our previous study is that the silica nanoparticles are pre-synthesized and dispersed in membrane casting solution rather than *in situ* formed through sol–gel process of silica precursor. The membrane pore size could be facilely controlled by adjusting the diameter of silica nanoparticles. In detail, the membrane casting solution was prepared by using HEMA as the monomer, benzoyl peroxide (BPO) as the initiator, 1, 6-hexanedioldiacrylate (HDODA) as the crosslinking agent and silica nanoparticles as the pore-forming agent. Two slide glasses were utilized to shape the casting solution into a flat sheet liquid film. With the free radical polymerization proceeding, the film evolved to polymeric network with silica nanoparticles embedding and finally solidified into the dense membranes. Porous membranes could be obtained through removing the silica nanoparticles from dense membranes. The morphologies, separation performances and antifouling properties of both porous polyHEMA and dense poly(HEMA/MAA)/SiO<sub>2</sub> membranes were investigated.

## 2. Experimental

### 2.1. Materials

Tetraethyl orthosilicate (TEOS), 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA) and benzoyl peroxide (BPO) were purchased from Kewei Chemical Reagent Co. (Tianjin, China). 1, 6-hexanedioldiacrylate (HDODA), methacryloxy propyl trimethoxyl silane (MPS) and poly(vinylphenol) were purchased from Aladdin Reagent Database Inc. (Shanghai, China). Bovine serum albumin (BSA) was obtained from Institute of Hematology, Chinese Academy of Medical Science (Tianjin, China). Dried yeast was purchased from Tianjin China–British Health Food Co. Ltd. and washed thoroughly with water and then dispersed in pure water prior to utilization. The commercial CA membranes (pore size 1.0 μm, thickness about 150.0 μm) were purchased from Shanghai Mili Membrane Separation Technology Co. Ltd (Shanghai, China). Water used in all experiments was prepared by Reverse Osmosis. All other chemicals were of commercially analytical grade.

### 2.2. Preparation of porous polyHEMA membranes

The silica nanoparticles were prepared *via* the Stöber method and were modified by MPS to enhance the dispersive property in

HEMA (Stöber et al., 1968). The average diameters of the synthesized silica nanoparticles were 60, 80, 100, 135 and 200 nm. Different amounts of silica nanoparticles were mixed with 2.0 g HEMA, 80.0 μL HDODA and 0.1 g BPO to prepare the membrane casting solutions. The addition amounts of silica nanoparticles were 320.0, 640.0 and 1280.0 mg, which rendered the  $W_{\text{SiO}_2}/W_{\text{HEMA}}$  value fixed at 16.0%, 32.0% and 64.0%, respectively. The mixture was stirred under supersonic for 5.0 min to make the silica nanoparticles well dispersed in the casting solution. In order to remove oxygen which may interfere the free radical polymerization, nitrogen gas was injected into the solution by pressure. Two slide glasses with the length of 75 mm and the width of 25 mm were first immersed in a poly(vinylphenol) (PVP) ethanol solution with the concentration of 20.0 mg/L. Then the slide glasses were taken out from the solution and dried at room temperature. In this way, a sacrificial layer was coated onto the surfaces of the slide glasses. After that, 20.0 μL of each casting solution was dripped and spread out onto one slide glass, which was then covered with the other slide glass. To confer certain pressure of 0, 0.65, 1.31, 1.96 and 2.62 KPa, the load with the weight of 0, 0.125, 0.25, 0.375 and 0.50 kg was put on the top slide glass, respectively. The slide glasses with the load were then put in an oven at  $80.0 \pm 1.0$  °C to implement thermal treatment for 24 h. After the two slide glasses were cooled to room temperature, they were uncoupled and immersed in ethanol. Subsequently, dense polyHEMA/SiO<sub>2</sub> membranes could be quickly peeled off the slide glass and the porous polyHEMA membranes could be obtained by transferring the dense membranes to a sodium hydroxide solution (0.1 mol/L,  $40.0 \pm 1.0$  °C) for 4 h to remove the silica nanoparticles within the membrane matrix. The resultant porous polyHEMA membranes were rinsed with ethanol and stored in pure water before use.

### 2.3. Preparation of dense poly(HEMA/MAA)/SiO<sub>2</sub> membranes

The casting solution for dense poly(HEMA/MAA)/SiO<sub>2</sub> membranes contained 2.0 g HEMA, 80.0 μL HDODA, 0.1 g BPO, different amounts of MAA (molar ratio to HEMA of 5.0 mol%, 10.0 mol% and 15.0 mol%) and 320.0 mg pre-synthesized silica nanoparticles with various average diameters of 60, 80, 100, 135 and 200 nm. The membrane formation process was the same as that of porous polyHEMA membranes but without removing silica nanoparticles.

### 2.4. Membrane characterization

The surface and cross-section morphologies of the membranes were observed by utilizing a field emission scanning electron microscope (FESEM, Nanosem 430). In order to produce electric conductivity prior to SEM analysis, the membrane samples frozen in liquid nitrogen were broken and sputtered with gold.

X-ray photoelectron spectroscopy (XPS, PHI-1600 X-ray photoelectron spectrometer, USA) was used to investigate the chemical compositions of the membrane surfaces. Mg Kα (1254.0 eV) was used as radiation source and the take-off angle of the photoelectron was set at 90°. Surface spectra of the membranes were collected over a range of 0–1100 eV.

To evaluate the hydrophilicity of the membranes, the static water contact angles of the membrane surfaces were measured. A contact angle goniometer (JC2000C Contact Angle Meter, Powereach Co., Shanghai, China) was used to carry out the measurement at room temperature. The membrane samples were lyophilized for 3 h and pressured to be plain with a rolling machine. A water droplet with a volume of 5 μL was dripped on the membrane surface with a microsyringe. At least six contact angles at different locations on one sample were averaged to acquire a reliable value.

To measure the porosity of the porous polyHEMA membranes, the superficial water of the membrane samples was first removed

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