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# Thermally induced phase separation followed by in situ sol–gel process: A novel method for PVDF/$SiO_2$ hybrid membranes

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ABSTRACT

Poly(vinylidene fluoride) (PVDF)/silica ($SiO_2$) hybrid membranes have been prepared by the thermally induced phase separation (TIPS) of PVDF/dimethyl sulfone ($DMSO_2$)/tetraethoxysilane (TEOS) followed by an in situ sol–gel process of TEOS. The two-steps rout integrates the enrichment of TEOS by TIPS and the hydrolysis of TEOS by in situ sol–gel reaction. As a result, two types of pores are obtained in the membranes: large tubular pores shaped by $DMSO_2$ crystals and small round pores stemming from TEOS droplets. In fact, the TEOS droplets can be 'hatchery' where $SiO_2$ particles are in situ generated by simply immersing the nascent membranes in an ethanol/ammonia solution for 12 h. Both FESEM images and energy dispersive X-ray analysis confirm that the $SiO_2$ particles are uniformly dispersed inside the PVDF/$SiO_2$ hybrid membranes, and their size and shape are well consistent with those of the small round pores. This integrating hybrid structure endows the membranes with high comprehensive properties including surface hydrophilicity, pure water flux, anti-compression property and mechanical strength. Moreover, the PVDF/$SiO_2$ hybrid membranes can be used to separate protein mixture (bovine serum albumin (BSA) and bovine hemoglobin (BHb)) based on electrostatic interactions, and pH 5.9 is the optimal condition. This work provides a novel method to prepare organic – inorganic hybrid membranes for potential applications in the fields of immunological analysis and membrane chromatography.



## 1. Introduction

Organic–inorganic hybrid materials have been extensively investigated as a promising choice for separation membranes [1–3]. The hybrid membranes usually show attractive advantages including expected separation performances, excellent mechanical properties, and high thermal and chemical stabilities [4–6]. These advantages are believed to be originated from the synergistic effects of the organic phase and the inorganic component. Therefore, the hybrid membranes have received intense attention in the fields of separation science [7–9], gas transportation [10,11], heterogeneous catalysis [12–14] and fuel cells [15–17]. For example, Pereira et al. [18] found that significant improvement can be obtained in ionic exchange capacity and proton conductivity by hybridizing Nafion membrane with mesoporous silica ($SiO_2$) containing sulfonic acid groups. Liang et al. [19] blended poly(vinylidene fluoride) (PVDF) matrix with nano-ZnO to optimize the membrane pores, and the hybrid membranes then exhibited excellent anti-irreversible fouling property. Saxena et al. [20] prepared poly(vinyl alcohol)/$SiO_2$ organic–inorganic hybrid membranes with charges to efficiently separate protein mixtures under coupled driving forces.

Inorganic particles are the most useful ones to be incorporated into polymeric matrixes to form the hybrid membranes. Nanoparticles are preferred inorganics such as $CaCO_3$ [21,22], $TiO_2$ [23–25], $Al_2O_3$ [26,27], ZnO [28,29], and $SiO_2$ [30–32]. Generally, they are directly blended with polymers in solvents, and the resulting suspensions are transferred into a nonsolvent to induce phase separation. This route is known to be the simplest and well-used method to prepare the hybrid membranes. However, the direct blending/phase separation method is always difficult to avoid agglomeration of the nanoparticles, especially in those cases with high particle content. Particle agglomeration causes large defects and limits the improvement of membrane performance. Recently, the sol–gel process, as a classic way for the nanoparticle formation of $SiO_2$ [33,34], has been introduced to combine with phase separation to prepare organic–inorganic hybrid membranes [35,36]. In the multiple processes, hydrolysis and polycondensation reactions take place to form nanoparticles in the presence of polymer networks during membrane formation. The confined growth of nanoparticles in polymer matrix can effectively prevent the aggregation of nanoparticles and control the final particle size. Xu et al. [37] prepared PVDF/$SiO_2$ hollow fiber membranes by combining the sol–gel process of tetraethoxysilane (TEOS) with the

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wet-spinning method. The in situ formed $SiO_2$ particles were homogenously dispersed in PVDF matrix, and apparently improved the mechanical property, thermal stability, permeation and antifouling performance of the hybrid membranes. However, by far, the sol–gel process is always combined with the nonsolvent induced phase separation (NIPS) method, which limits the development of hybrid membranes undoubtedly. Thermally induced phase separation (TIPS) is known to be another useful method for the preparation of porous membranes. Compared to NIPS, TIPS has several advantages such as ease of control, low tendency to defect formation and ease to fabricate diverse microstructures, which are desirable for various applications of membrane. Accordingly, TIPS has been applied to many polymers including PVDF [38–40], polyethylene [41,42], polypropylene [43–45], and polyacrylonitrile [46–49]. To our best knowledge, no literatures have reported the combination of TIPS and the sol–gel process of TEOS to prepare organic–inorganic hybrid membranes based on polymers and $SiO_2$ particles. One remaining challenge is that the sol–gel process is still difficult to take place simultaneously during the cooling step of TIPS. It is well known the sol–gel process of TEOS is always performed with a basic aqueous medium. Therefore, a two-steps method is required to overcome the challenge as mentioned above, that is, TIPS followed by the sol–gel process of TEOS. Nevertheless, the normally used diluents in TIPS and TEOS are usually liquid at room temperature. TEOS prefers to elute out when immersing the nascent membrane into the aqueous reaction solution, which makes the sol–gel process unfulfilled in the organic matrix.

In this work, organic–inorganic PVDF/$SiO_2$ hybrid membranes were prepared via TIPS followed by the sol–gel process of TEOS. Dimethyl sulfone ($DMSO_2$) was used as a crystallizable diluent. It crystallizes into solid upon cooling, which can hold TEOS in the diluent phase, ensure the sol–gel process happens inside the membrane matrix, and reduce the loss of formed $SiO_2$ particles. We report the effects of TEOS content in the binary diluent system on the pore size, surface porosity, overall porosity, surface hydrophilicity, water flux as well as mechanical properties of the prepared hybrid membranes. The stability of water flux under high pressure was used to characterize anti-compression property of the hybrid membranes. Furthermore, initial protein separation studies were conducted with the as-prepared membranes. Bovine serum albumin (BSA, $pI=4.7$, $M_w=66$ KDa) and bovine hemoglobin (BHb, $pI=7.0$, $M_w=64.5$ KDa), which have nearly identified molecule weight, were selected as model proteins.

## 2. Experimental

### 2.1. Materials

PVDF ($M_n=110{,}000$ g/mol, Solef 6010) is a commercial product of Solvay Solexis, Belgium. It was dried to constant weight before use. $DMSO_2$ (99%) was purchased from Dakang Chemicals Co., China. Tetraethoxysilane (TEOS), ethanol ($C_2H_5OH$), ammonium hydroxide (28 wt%, $NH_3\cdot H_2O$), *N*,*N*-dimethylformamide (DMF), disodium hydrogen phosphate ($Na_2HPO_4\cdot 12H_2O$), potassium dihydrogen phosphate ($KH_2PO_4$), sodium chloride (NaCl), bovine serum albumin (BSA, $pI=4.7$, $M_w=66$ KDa) were supplied by Sinopharm Chemical Reagent Co. Ltd., and used without further purification. Bovine hemoglobin (BHb, $pI=7.0$, $M_w=64.5$ KDa) was obtained from Beijing Biodee Biotechnology Co., Ltd., China. Ultrapure water (18.2 MΩ) was purified by an ELGA LabWater system (France). Deionized water was used as the extractant.

### 2.2. Determination of phase behavior

The phase separation process was visualized by an optical microscope (Nikon Eclipse E600POL, Japan). PVDF, $DMSO_2$ and TEOS were weighed in a certain mass ratio, and mixed in a glass vessel. The mixture was heated at 150 °C with vigorous stirring to form a homogenous solution. Then the solution was quenched into a liquid nitrogen bath, and a solid PVDF/$DMSO_2$/TEOS mixture was yielded. A small section of the solid mixture was placed between a pair of microscope slides, and put on a hot stage (Linkam TMS-93) with a temperature controller (Linkam THMS-600). The sample was heated to 150 °C at 30 °C/min, maintained for 1 min, and then cooled to 25 °C at 10 °C/min. The vision field was recorded at the moment of solidification.

Differential scanning calorimetry (DSC, Q1000, TA instruments, USA) was used to determine the crystallization and melting behaviors of PVDF/$DMSO_2$/TEOS mixtures. The procedure and parameters were similar to our previous work [48].

### 2.3. Preparation of PVDF/$SiO_2$ hybrid membranes

PVDF/$DMSO_2$ mixture was first heated at 150 °C to form a homogeneous solution. A certain amount of TEOS was then added directly into the solution under continuous agitation. After degassing air bubbles, the cast solution with TEOS loading of 0, 5, 10, 15 and 20 wt% (the weight percentage to the mixed diluent) was quickly poured onto a stainless steel mold (thickness ~200 μm), which was preheated in an oven at 150 °C. The mold was then quenched in a water bath at 30 °C to induce the solution to phase separation. Thus a solidified nascent membrane was formed containing liquid TEOS inside. Afterward, the obtained nascent membrane was taken out of the mold and immediately immersed in an $NH_3\cdot H_2O/C_2H_5OH$ solution ($C_2H_5OH/NH_3\cdot H_2O$/TEOS = 40/2/1, vol/vol/vol). A sol–gel

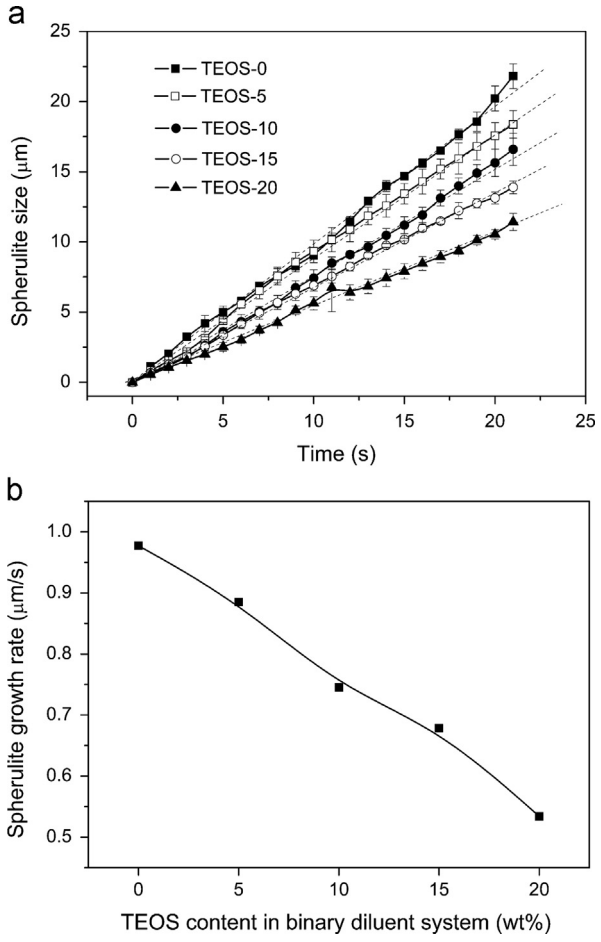


**Fig. 1.** Time-dependent spherulite size of PVDF/$DMSO_2$/TEOS ternary system with different TEOS contents.