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Regular Article

Fabrication of mesoporous titania–zirconia composite membranes based on nanoparticles improved hydrosol

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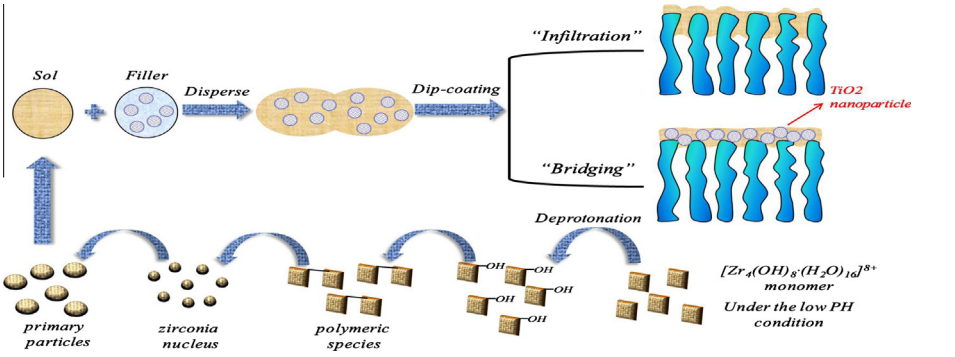
HIGHLIGHTS

- The sols infiltration and film cracking were effectively suppressed by the bridging effect of the nanoparticles.
- Diethanolamine could retard ZrO_2 tetragonal-to-monoclinic phase transition.
- After doping nanoparticles into the hydrosol, the prepared membrane showed improved performance.
- A novel method to prepare TiO_2—ZrO_2 composite membranes or even other composite functional membranes was suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method for the fabrication of mesoporous titania–zirconia (TiO_2—ZrO_2) composite membranes was successfully developed based on nanoparticles (NPs) improved hydrosol. ZrO_2 hydrosols were synthesized through a straightforward sol–gel route using zirconium oxychloride. Compared to the polymeric sol route, this method was found to be more environmentally friendly because organic solvent was not required. Further, highly hydrophilic TiO_2 NPs of 10–20 nm were well dispersed in the sol and effectively reduced the sol infiltrating into the channels of the support layer by a "bridging" effect. After a rapid evaporation process, a mixed matrix gel was formed on the surface of the support. The dynamic mechanical analysis results showed that the toughness and stiffness of the gel were significantly strengthened, which was beneficial to reduce the risk of membrane cracking. So, an integrated, crack-free mesoporous TiO_2—ZrO_2 composite membrane was obtained by directly coating and sintering the mixture on a macroporous support. It showed that the composite membrane delivered better separation performance though the filtration test. The water flux, molecular weight cutoff, and average pore size of the synthesized membrane were 60 L m^{-2} h^{-1} bar^{-1}, 4704 Da, and 3.5 nm, respectively.

1. Introduction

Mesoporous ceramic membranes, especially ZrO_2 and TiO_2 membrane with pores between 2 and 50 nm size, have a fine ultrafiltration performance for the separation and purification of macromolecules and colloids, and have been applied in water treatment, pharmaceutical, and food industries [1–6]. In order to obtain some specific functions, such as catalytic activity and proton conductivity, novel mesoporous ceramic composite membranes have been explored and successfully developed [7,8]; however, construction

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and control of the microstructure of the composite membranes have still been a challenging task.

The sol–gel method is considered to be extremely practical for fabricating mesoporous ceramic membranes. And the microstructure of the membrane materials and performance of membranes are largely determined by the surface and pore structure of the support, the properties of the sol, and the drying and sintering conditions [9–11]. The hydrosols derived from inorganic salt are more environmentally friendly and economical to prepare ZrO_2 and TiO_2 mesoporous membranes compared to the polymeric sols [5,6,12,13]. However, as far as fabrication of ceramic composite membranes is concerned, it is extremely difficult to obtain a stable mixed hydrosol since flocculation might occur if the surface charges on the sol particles are of the opposite sign [14]. Habibpanah et al. [15] successfully prepared TiO_2—Al_2O_3 composite sol by co-hydrolysis of the precursor mixture, though it was time-consuming and complicated to accurately dominate temperature in different periods. Hao et al. [16] fabricated ZrO_2—Al_2O_3 composite membranes via mixing boehmite sol and ZrO_2 sol at pH of about 3.7. In that case, the composition ratio of composite sols must be strictly controlled in a precise range in order to obtain a stable and transparent sol.

Moreover, when the hydrosols are coated on the surface of a macroporous support to obtain an unsymmetrical membrane with a better mechanical strength and filtration performance, the infiltration of the sols into the channels of the support becomes inevitable. In general, one or more transition layers with narrower pore size distribution and smaller pore size have to be adopted to reduce the infiltration; however, this results in an increase in filtration resistance. A number of related researches have been focused on the fabrication of crack-free films on the macroporous support. For instance, the fabrication of fiber transition layer on the support avoided sol particles infiltrating into the support; however, it also caused desquamation of the layer [17,18].

Another problem related to the direct coating of the sols on the macroporous support involves the easy cracking of the film on an uneven surface during the film drying and sintering process. In our previous study, the TiO_2 polymeric sol with 0.3 g L^{-1} P25 nanoparticles (NPs) was selected as an ideal candidate for preparing membranes [19]. The result of dynamic mechanical analysis showed that the NPs toughened the polymeric sols, which improved the film mechanical properties and resulted in the formation of integrated crack-free films. A reduction in risk of film cracking caused by the uneven shrinkage stress distribution on a rough surface was observed. Thus, addition of NPs can toughen the film of the composite materials.

Herein, we proposed a novel method that combined the NPs toughening technology with the eco-friendly hydrosol method for the preparation of mesoporous TiO_2—ZrO_2 composite membranes on macroporous support. The ZrO_2 hydrosol was prepared via aqueous sol–gel route with diethanolamine (DEA) as the chelating agent for controlling hydrolysis–condensation process. The hydrophilic TiO_2 NPs with size of 10–20 nm uniformly dispersed in the ZrO_2 hydrosol which settled the question of flocculation due to destabilization during the mechanical mixing of TiO_2 and ZrO_2 sols. The effect of NPs on the hydrosol and gel properties, the microstructure of the membrane materials, and membrane performance have been systemically reported.

2. Experiments

2.1. Synthesis of TiO_2—ZrO_2 binary hydrosol

Zirconium oxychloride (6.44 g) and $Y(NO_3)_3{\cdot}6H_2O$ (0.61 g) were dissolved in water (50 mL), and then 0.005, 0.01, 0.015, and 0.02 mol DEA was, respectively, added drop-wise to the solution kept at 85 °C while stirring at high speed for 6 h. Moreover, $Y(NO_3)_3{\cdot}6H_2O$ acted as a crystal phase stabilizer during the preparation of membrane [20,21]. Then, TiO_2 NPs of size 10–20 nm (produced by Anhui Xuancheng Jingrui New Material Co., Ltd) were added into the prepared hydrosol and a stable mixture of a Ti/Zr molar ratio of 0%, 10%, and 20% was obtained by stirring for 2 h followed by ultrasonic dispersion for 30 min at 250 W, respectively. Finally, polyvinyl alcohol (PVA, 0.5 wt%) was used to enhance the viscosity of the mixture and prevent the cracking of membrane layer during the drying step.

Fig. 1 shows the proposed mechanism for the formation process of TiO_2—ZrO_2 binary hydrosol. The NPs in the hydrosol primarily settled on the surface of the tubular support and played a 'bridging' role during the dip-coating process, according to the mechanism of filtration and capillary action, which could effectively retard the hydrosol particles infiltrating into pore channels of the support. During the drying and sintering process, evaporation of water and contraction of the gel volume, capillary force occurs, resulting in the deformation of gel network, internal pore collapse, and even film cracking, because wet gel has a large gap in the internal structure of the network. The prepared hydrosol with small amount of PVA showed the properties of the polymer in gel state. Therefore, based on the mechanism of NPs toughening polymer [22,23], the NPs helped in avoiding film cracking because they resisted the uneven shrinkage stress distribution.

2.2. Synthesis of membrane

Tubular macroporous ZrO_2 support membrane (8 mm in inner diameter, 110 mm in length, and 2 mm in wall thickness) was prepared by the Membrane Science & Technology Research Center (Nanjing, China). The pore size distribution of support membrane was determined by gas bubble pressure method. Fig. 2 shows the support membrane with a maximum pore size of 1.15 μm and an average pore size of 180 nm. Also the most probable pore size is equal to the average pore size. The membrane layer was formed by dip-coating on the inner surfaces of the tubular support in the prepared composite sol, while the circulation process continuing by a wriggle pump. The coated tubes were dried at 60 °C for 12 h, followed by calcination in air at 500 °C for 4 h. Heating rate of 0.5 °C min^{-1} and cooling rate of 1 °C min^{-1} were chosen. After four times of repetition, the TiO_2—ZrO_2 composite membranes were obtained finally.

2.3. Characterization

The viscosity of the sol was determined using a rotary viscometer (DV-II+, Brookfield, USA) at 30 °C. Particle size and size distribution of prepared sols were measured by the phase analysis light scattering technique (ZetaPALS, Brookhaven, USA). The mechanical properties of the formed gels were examined using dynamic mechanical analysis (DMA, Diamond DMA, Perkin-Elmer, USA), and the measurements were performed under tensile at an oscillating frequency of 1 Hz. A transmission electron microscope (TEM) (JEM-2100F, JEOL, Japan) was used to study the TiO_2 NPs morphology and grain size. The crystalline phase was examined by Wide-angle X-ray diffraction (WAXRD) by an X-ray diffractometer (Rigaku MiniFlex 600) with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 15 mA. The pure water flux and polyethylene glycol (PEG) retentions of the prepared TiO_2—ZrO_2 composite membrane were examined following the ASTM E 1343–90 standard procedure. A BELSORPII N_2 adsorption-desorption instrument was utilized to measure specific surface area and pore size of the membrane material. The specific surface area of the material were estimated by the Brunauer-Emmett-Teller (BET) equation. The pore size distributions was evaluated according to the