Materials Letters 232 (2018) 74–77

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

One-step synthesis of flower-like Si_2N_2O nanowires on the surface of porous SiO_2 ceramic membranes for membrane distillation

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ARTICLE INFO

Article history:
Received 29 May 2018
Received in revised form 14 July 2018
Accepted 7 August 2018
Available online 10 August 2018

Keywords:
Ceramics
Porous materials
Si_2N_2O nanowires
Super-hydrophobicity
Membrane distillation

ABSTRACT

SiO_2 porous ceramic membrane was prepared through phase inversion tape casting and pressureless sintering method. Flower-like Si_2N_2O nanowires was *in-situ* formed on the surface of the SiO_2 membrane, in NH_3 atmosphere, through vapor–solid (VS) process. Once modified by inorganic SiNCO film, super-hydrophobicity of the membrane with a water contact angle (WCA) of 160° was achieved, which showed high chemical and thermal stability. The prepared membrane had a very good performance in membrane distillation (MD) experiments, with water flux as 11.11 $L{\cdot}m^{-2}{\cdot}h^{-1}$ and >99.9% salt rejection for 4 wt% NaCl aqueous solution at 90 °C, which was kept stable in harsh conditions.

1. Introduction

Membrane distillation (MD) attracts great interest in water desalination technology. Porous ceramic membranes satisfactorily meet the requirements of MD because of their high porosity, suitable pore size distribution, and high mechanical strength, as well as thermal and chemical stability [1–3]. In order to prevent the liquid water diffusion through the membrane structure in MD process, materials with low surface energy, such as the fluoroalkylsilane (FAS) and stable SiNCO inorganic coating have been used to transform the surface of the ceramic membrane from intrinsic hydrophilicity to hydrophobicity [4]. But the long-term stability and membrane fouling have remained as challenges [5]. To further enhance hydrophobicity and anti-fouling properties, several methods, which aim to increase the surface roughness of ceramic membranes, have been developed [6–8].

Silicon oxynitride (Si_2N_2O), which displays strong resistance against oxidation, high mechanical strength, and low thermal conductivity, has been intensively investigated as a high temperature functional engineering material [9]. Its structure is similar to that of stable SiNCO inorganic coating. This fact should clearly favor the growth of a layer of silicon oxynitride nanowires on the membrane surfaces, enabling the increase of the surface roughness and the establishment of a strong bonding between the coating and the substrate.

This work presents a novel one-step synthesis of flower-like Si_2N_2O nanowires forming *in-situ* on the surface of SiO_2 porous ceramic membranes. After coating with inorganic SiNCO nanoparticles, the resultant membrane was expected to display super-hydrophobicity features. Finally, the stability and application of the prepared membrane were evaluated.

2. Material and methods

Briefly, 40.0 g starting powder mixture consisting (in wt%) of 93% SiO_2, 2% Al_2O_3 and 5% Y_2O_3, 5.7 g polyethersulfone (PESf) and 0.8 g polyvinylpyrrolidone (PVP) were dissolved in 31.0 g N-methyl-2-pyrrolidone (NMP) to form a stable ceramic slurry. After degassing, the slurry was tape-casted with a doctor blade of a 1 mm gap. Phase-inversion was carried out by immersing the membrane in a tap water for 12 h. After drying at room temperature, the green tape was placed in a furnace and fired at 1400 °C for 4 h in flowing NH_3 (99.6%) gas at a flow rate of 0.3 L min^{-1}.

Then, the membranes were hydrophobic modified. More specifically, the membranes were immersed in a solution, where 1 ml dimethyldichlorosilane and 1 ml dichloromethylsilane dissolved in 5 ml n-heptane. Then, the membranes were placed in a porcelain boat and transferred to a box-type resistance furnace, followed by heating at 320 °C for 0.5 h and finally 600 °C for 1 h.

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https://doi.org/10.1016/j.matlet.2018.08.043
0167-577X/

The morphologies of the membranes were observed by the scanning electron microscope (SEM, JEOL JSM-6390LA) and a high resolution transmission electron microscope (HRTEM, JEOL JEM-2100F). Phase analysis was evaluated by X-ray diffraction (XRD, Philips PW 1700). Water contact angle was measured using a contact angle meter (SL200B, Solon Tech Co., Ltd.). The pore size distribution and porosity of prepared membrane were measured by the bubble method and Archimedean. Water desalination experiments were carried out using a sweeping gas membrane distillation (SGMD) pilot as shown in Fig. 4A and B.

3. Results and discussion

The structural and crystallographic features of the membranes produced were summarized in Fig. 1. More specifically, the cross-section shown in Fig. 1A indicated a typical asymmetric membrane structure, which consisted of a layer of open, long and straight finger-like voids, formed between a sponge layer, with a thickness of ~100 μm, and a very thin skin layer [10]. A flower-like microstructure of nanowires, grown out of several central points, covered the membrane surface (Fig. 1B and C). This kind of special surface structure can be easily modified to hydrophobic. The measured average pore diameter of the membrane surface was 0.81 μm, which meet the requirements of membrane distillation [1]. The measured porosity of 49% combined with the pore structure will greatly benefit the mass transfer. The X-ray diffractograms of membrane surface with the main peaks correspond to that of Si_2N_2O, shown in Fig. 1D, suggested that the flower-like Si_2N_2O dominated the phase composition of membrane surface. For the inner part of the membrane, pure SiO_2 phase remained, which provide the membrane strength.

The characterization of the flower-like structure by HRTEM (Fig. 2A) showed that the nanowires had a uniform width along their entire length and were well crystallized (inset of Fig. 2A-a; the ripple-like contrast might be due to strain owing to the bending of the nanowires). The *d* space was measured as 0.48 nm, which was a good match to the (0 0 1) plane of Si_2N_2O. This suggested that the nanowire should grow along the [0 0 1] direction. The element mapping, shown in Fig. 2A-b, suggested that the nanowires were comprised of uniformly dispersed Si, N, and O.

The formation of Si_2N_2O nanowires should take place via the vapor–solid (VS) growth mechanism [11–14], which was schematically represented in Fig. 2B. In the initial stage, SiO_2 reacted with NH_3 to form Si_2N_2O polycrystal seed by Eq. (1) at different sites of the membrane surface, which would play the role of template in the following process. Then gaseous SiO was generated through Eq. (2) and reacted with the flowing NH_3 gas on the surface of the polycrystal Si_2N_2O seeds, based on Eq. (3). Because crystal growth of [0 0 1] direction was much faster than the other dimensions, nanowires should radially grow from the surface of the polycrystal Si_2N_2O seeds to form flower-like morphology, leading to a flower-like morphology. The Gibbs free energies of Eqs. (1), (2), and 3 are −126.778, −126.919, and −219.117 kJ mol^{-1}, confirming the thermodynamic feasibility of the reactions.

$$2SiO_2(s) + 2NH_3(g) \rightarrow Si_2N_2O(g) + 3H_2O(g) \quad (1)$$

$$SiO_2(s) + 2NH_3(g) \rightarrow SiO(g) + H_2O(g) + N_2(g) + 2H_2(g) \quad (2)$$

$$2NH_3(g) + 2SiO(g) \rightarrow Si_2N_2O(s) + H_2O(g) + 2H_2(g) \quad (3)$$

This flower-like microstructure increased the roughness of membrane surface, therefore, hydrophobicity increased. Indeed, the produced membrane displayed a super-hydrophobic behavior, with a WCA of ~160°. The membrane surface has excellent chemical stability, since these wetting properties were perfectly maintained even after immersion of the membranes in different solutions, 0.01 M HCl and 0.001 M NaOH aqueous solutions, specifically, as well as benzene up to 24 h (Fig. 3A). The membrane surface had very good thermal stability, as well, since it remained highly hydrophobic (WCA > 150°) after an 1-hour exposure to air at high temperatures up to 400 °C (Fig. 3B). A decay of WCA was

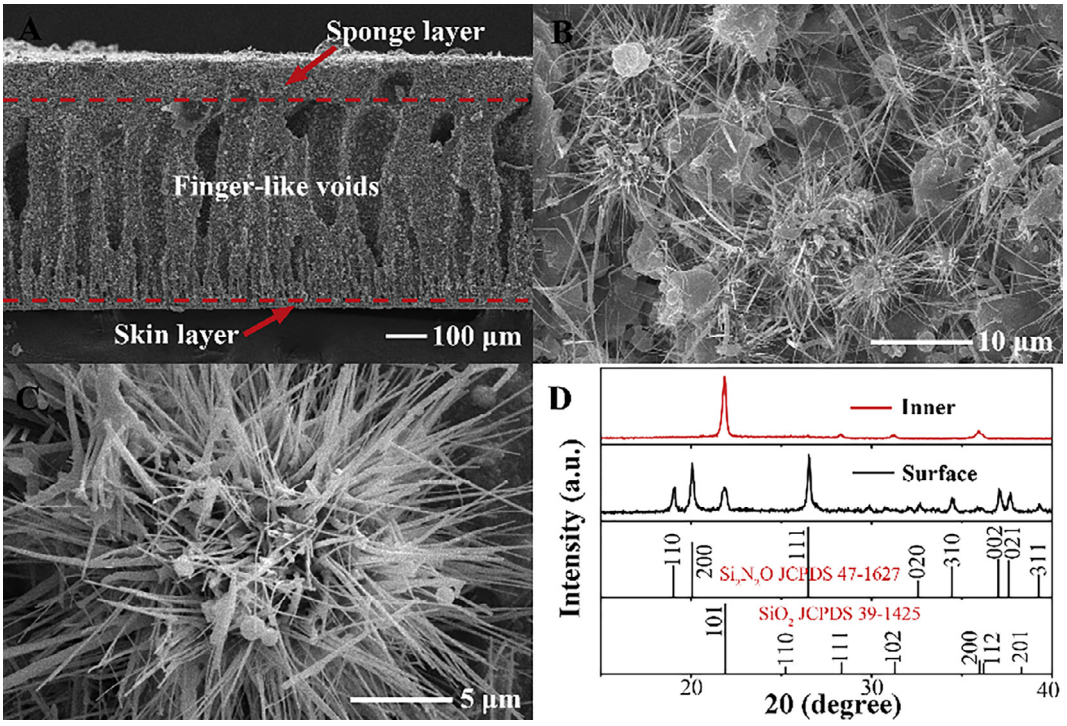

Fig. 1. Cross-section (A), top view of the surface of the membranes (B and C), and X-ray diffractograms of the inner and the surface of the membrane (D).