

Electronic Supplementary Information (ESI) for

Formation of continuous and high permeable ZIF-8 membranes on porous alumina and zinc oxide hollow fibers

Xiaobin Wang^{a*}, Mingyong Sun^a, Bo Meng^a, Xiaoyao Tan^b, Jian Liu^c, Shaobin Wang^c and Shaomin Liu^{c*}

1. Experimental details

1.1 Preparation of Al₂O₃-ZnO composite hollow fibers

The hollow fiber precursor was prepared by phase inversion technique followed by high temperature sintering. Firstly, 80 wt.% Al₂O₃ and 20 wt.% ZnO powder was uniformly dispersed by mixing in ethanol solution via ball milling. Secondly, a homogeneous suspension of approximately 59.3 wt.% Al₂O₃-ZnO powder, 7.4 wt.% polyethersulfone (PESf), 29.6 wt.% 1-methyl-2-pyrrolidinone (NMP) and 3.7 wt.% polyvinyl pyrrolidone (PVP, K30) was obtained under vigorous stirring. Subsequently, the hollow fiber precursors were obtained by the phase inversion method. The spinning process was carried out at room temperature through a spinneret using water and a mixture of NMP and ethanol as the external and internal coagulants. More details of the spinning process can also be found elsewhere [1-5]. The hollow fiber precursors were dried and finally sintered at 1550 °C for 4h in a tubular furnace. The pure Al₂O₃ hollow fiber without ZnO was also prepared in a similar procedure.

1.2 Preparation of ZIF-8 membranes

The Al₂O₃-ZnO hollow fiber support was firstly placed in a 0.5M Hmim (2-methylimidazole) and methanol (MeOH) solution at 333 K for 4h to activate the support and produce nucleation sites. The required zinc nitrate solution was prepared by dissolving 2g Zn(NO₃)₂·6H₂O and 0.46g HCOONa in 62mL methanol and meanwhile Hmim solution was obtained by adding 0.8g of Hmim in 60mL methanol, both of which were mixed and referred as the synthesis solution. The hollow fibers were then immersed inside the synthesis solution with a final molar ratio of 1 Zn(NO₃)₂:1.5 Hmim:450 MeOH:0.65 HCOONa in a Teflon vessel, sealed in a stainless steel autoclave and placed in a 373K oven for ZIF-8 membrane growth. After crystallization for 6h at 373K, the membranes were washed thoroughly in methanol and dried at 50 °C for 24 h. The membranes supported on the bare Al₂O₃ hollow fibers were also prepared for comparison purpose in a quite similar procedure but the activation step.

1.3 Characterizations

XRD analysis was conducted on a Bruker D8 Advance diffractometer using Cu-K α radiation ($\lambda = 0.1542$ nm) at 35 kV and 30 mA. The morphology of the supported membrane was ascertained by field emission scanning electron microscopy (FESEM, FEI Sirion 200, Netherlands). The distribution of elements was detected by the energy dispersive X-ray (EDX) equipped on the SEM. The permeability of the membranes was tested in a home-made permeation cell at a pressure drop of 0.1 MPa using H₂, N₂, CO₂ and CH₄ gases. The feed stream was pressurized and the downstream pressure was maintained at atmospheric pressure. The gas permeation was measured by a soap film bubble flow meter.

Reference

- [1] X. Tan, S. Liu and K. Li, *J. Membr. Sci.*, 2001, **188**, 87.
- [2] S. Liu, X. Tan and K. Li, *J. Membr. Sci.*, 2001, **193**, 249.
- [3] X. Tan, Y. Liu and K. Li, *Ind. Eng. Chem. Res.* 2005, **44**, 61.
- [4] X. Meng, N. Yang, X. Gong, Y. Yin, Z. Ma, X. Tan, Z. Shao and S. Liu, *J. Mater. Chem. A*, 2015, **3**, 1017.
- [5] J. Song, B. Meng, X. Tan and S. Liu, *Int. J. Hydrogen Enegr.*, 2015, **40**, 6118.

2. XRD patterns of hollow fibers

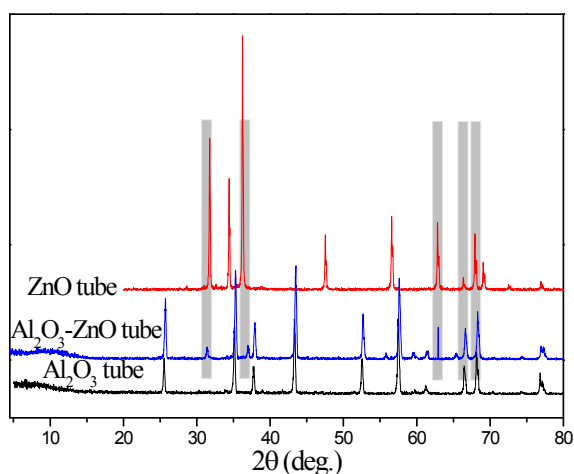


Fig. S1 The XRD patterns of pure Al₂O₃, ZnO and Al₂O₃-ZnO composite hollow fibers.

3. ZIF-8 membrane supported on pure Al₂O₃ hollow fibers

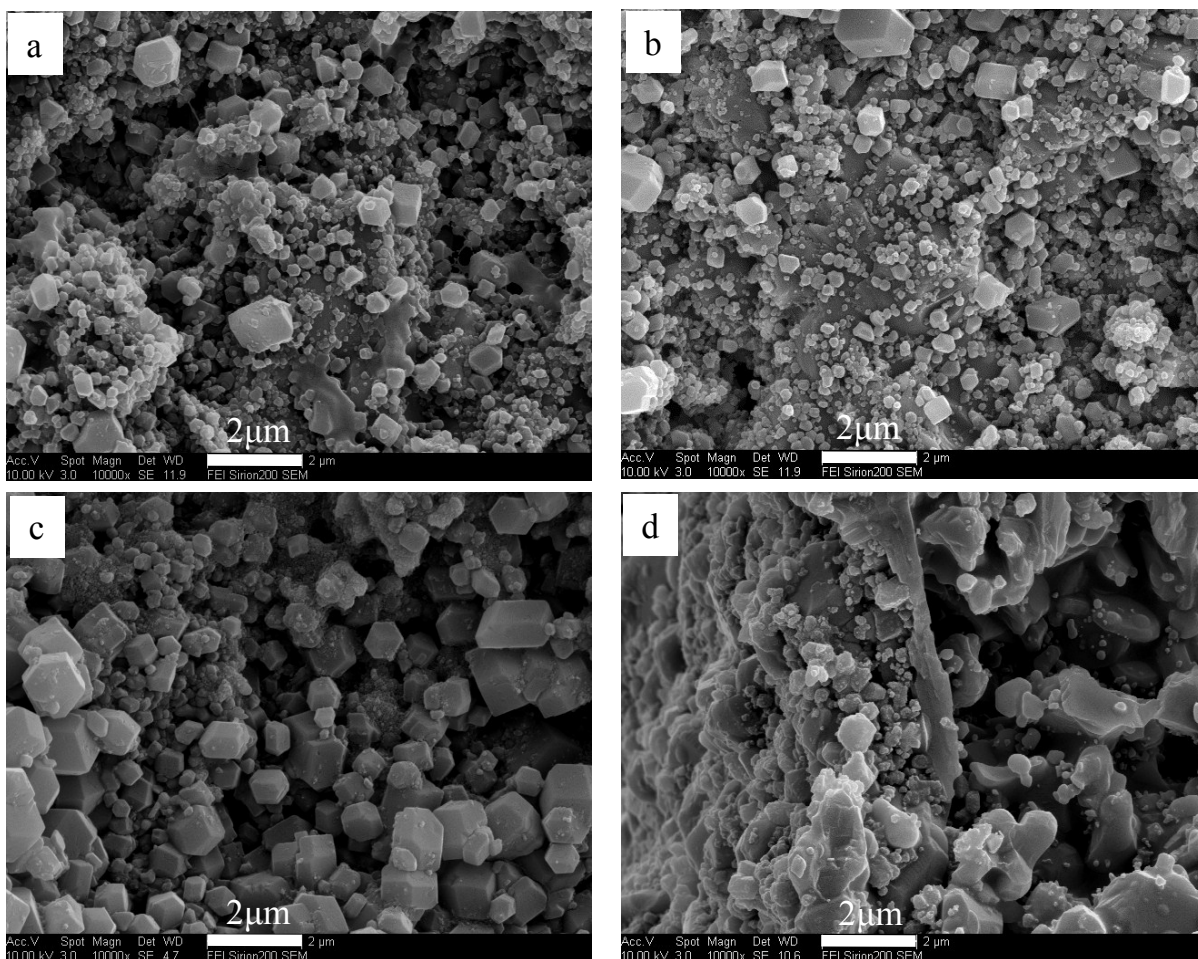


Fig. S2 SEM images of ZIF-8 membranes deposited on the pure Al_2O_3 support with different synthesis cycles (a: one; b: two; c,d: three).

4. ZIF-8 membrane supported on pure Al_2O_3 -ZnO composite hollow fibers without activation

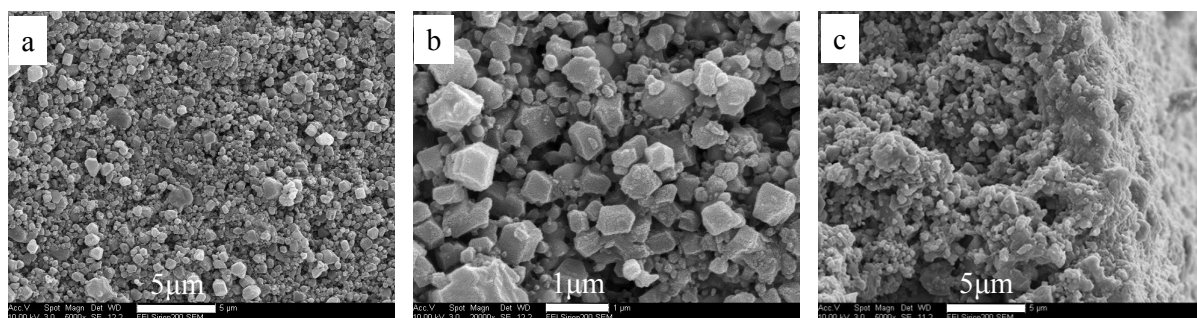


Fig. S3 SEM images of ZIF-8 membranes (a,b: surface; c: cross-section) deposited on the Al_2O_3 -ZnO composite hollow fibers without Hmim activation.