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Tailoring both the surface pore size and sub-layer structures of PVDF membranes prepared by the TIPS process with a triple orifice spinneret

Supplementary Information

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1. Changes in membrane morphology on changing the extruded solvent type

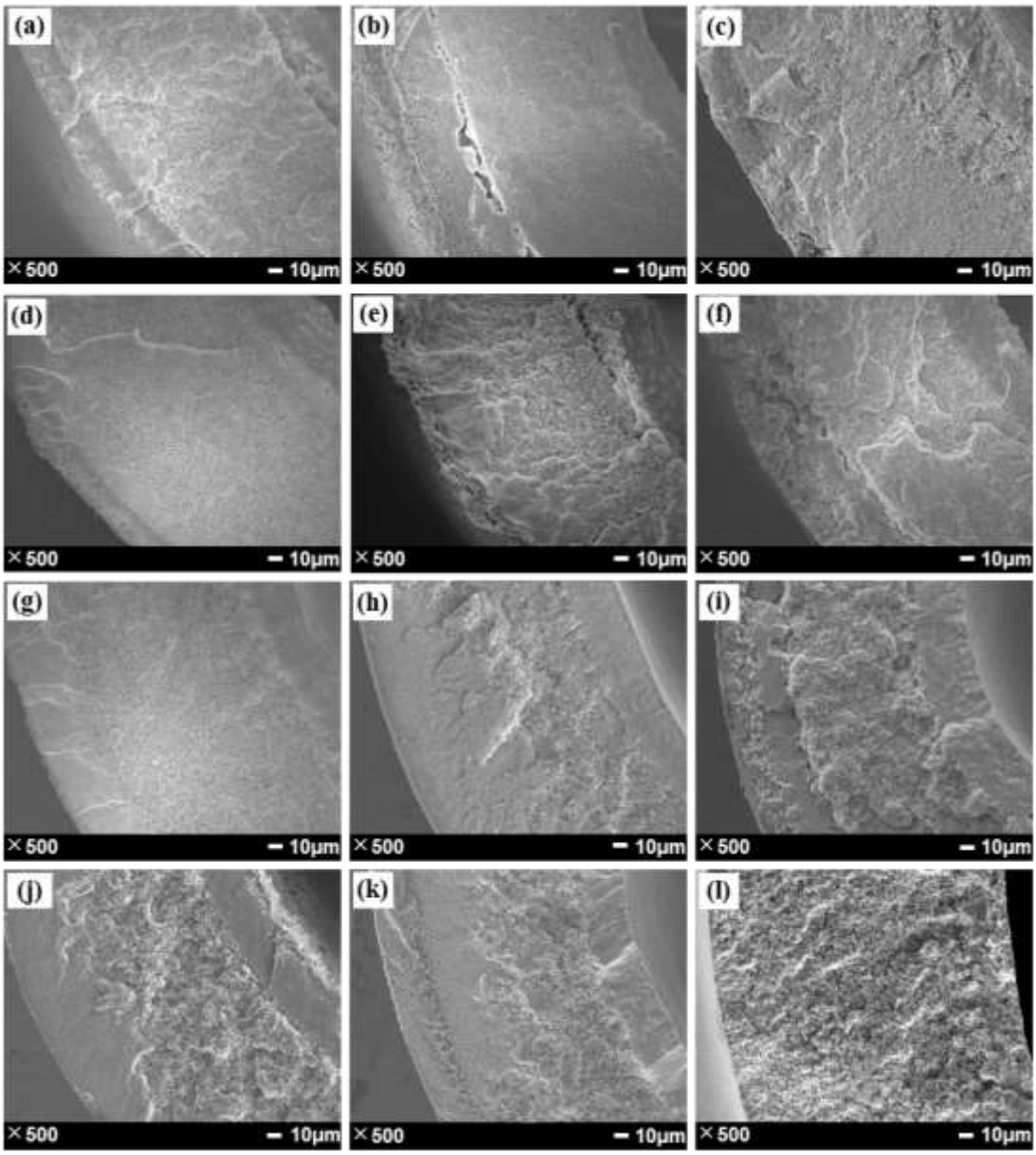

Fig. S1 Cross-sectional bulk SEM images of PVDF hollow fiber membranes prepared with different extruded solvents: (a) DEP, (b) TEP, (c) GTA, (d) ATBC, (e) DMP, (f) PC, (g) 1,3-butanediol, (h) GBL, (i) NMP, (j) GC and (k) glycerol, and (l) a normal PVDF hollow fiber membrane.

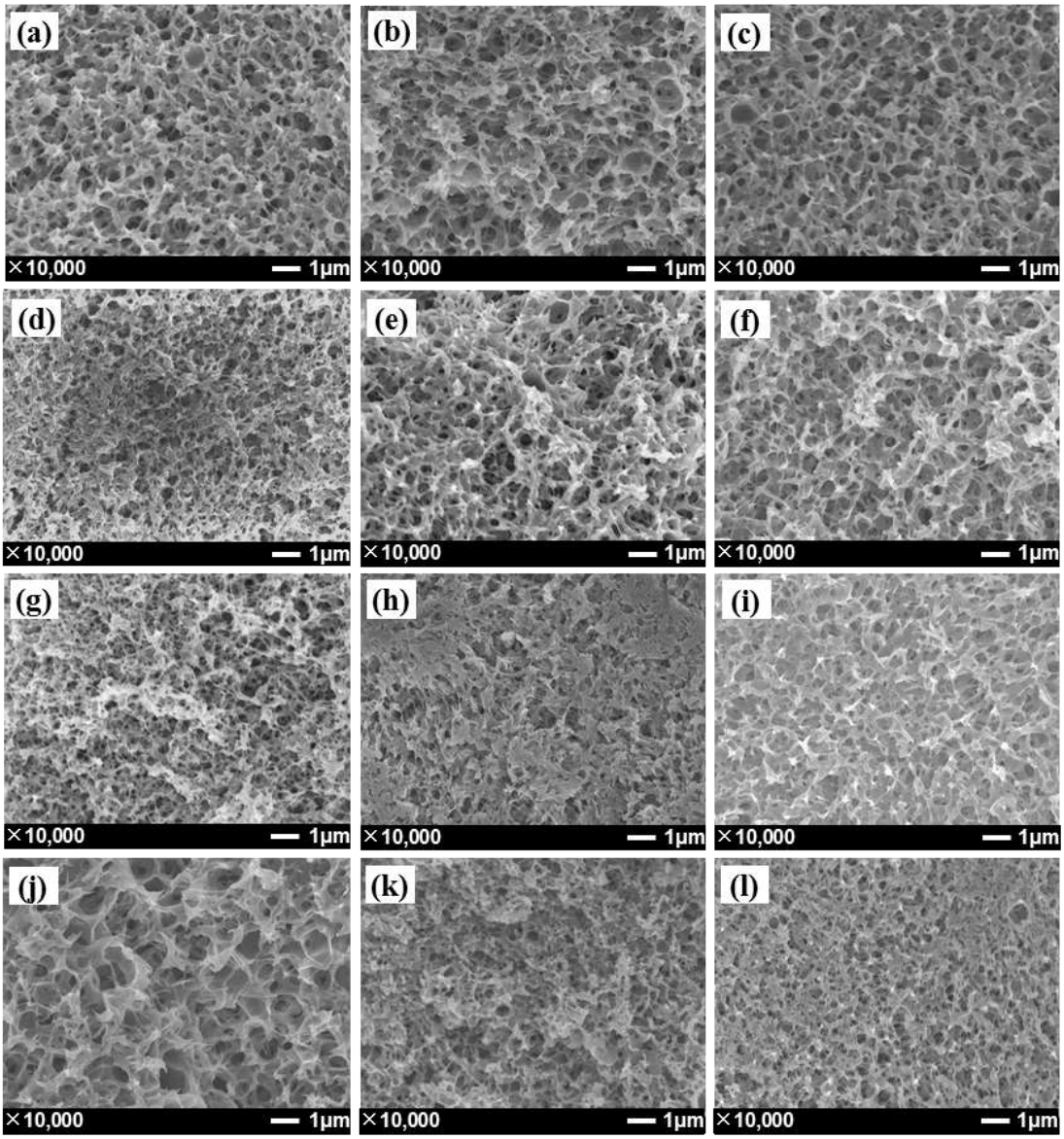

Fig. S2 Cross-sectional bulk SEM images around the center of the PVDF hollow fiber membranes prepared with different extruded solvents: (a) DEP, (b) TEP, (c) GTA, (d) ATBC, (e) DMP, (f) PC, (g) 1,3-butanediol, (h) GBL, (i) NMP, (j) GC and (k) glycerol, and (l) a normal PVDF hollow fiber membrane.

2. The effect of operation pressure on the permeation stability of the membranes

The effect of operation pressure on the permeation stability of the membrane was investigated and the results are shown in Figs. S3 and S4. Fig. S3 shows the variation trend in pure water permeability of the membranes as a function of filtration time at different pressures. In Fig. S3, the membrane prepared with extruded PC showed a highly stable pure water permeability regardless of the pressure, while the pure water permeabilities of the other three membranes decreased in different degrees. On the basis of these results, the effect of pressure on

permeation stability was summarized in Fig. S4 by using a parameter of the pure water permeability retention. In Fig. S4, the membrane prepared with extruded PC showed a high pure water permeability retention of more than 90% when the pressure increased up to 3 bar, indicating that the membrane had a high compressive resistance and could be used at high pressure. However, the other three membranes had a clear reduction in the retention of pure water permeability with increased pressure, showing a low permeation stability. The diversity in the permeation stability indicated that although the composite-like structure was formed at the sub-layers of four membranes, the compressive resistance of the membranes was different. In fact, in Fig. 3(b, e, f and i), it is exhibited that the spherulites constructing the composite-like structures were different, such as shape, size, number, etc. In addition, this novel composite-like structure showed different percentages in the whole membrane structures. However, until now, it is not clear which parameter plays a key role in further enhancing the permeation stability of PVDF membranes. Hence, it is necessary to investigate more deeply the effect of spherulites on the permeation stability of the membrane and then summarize critical factors.

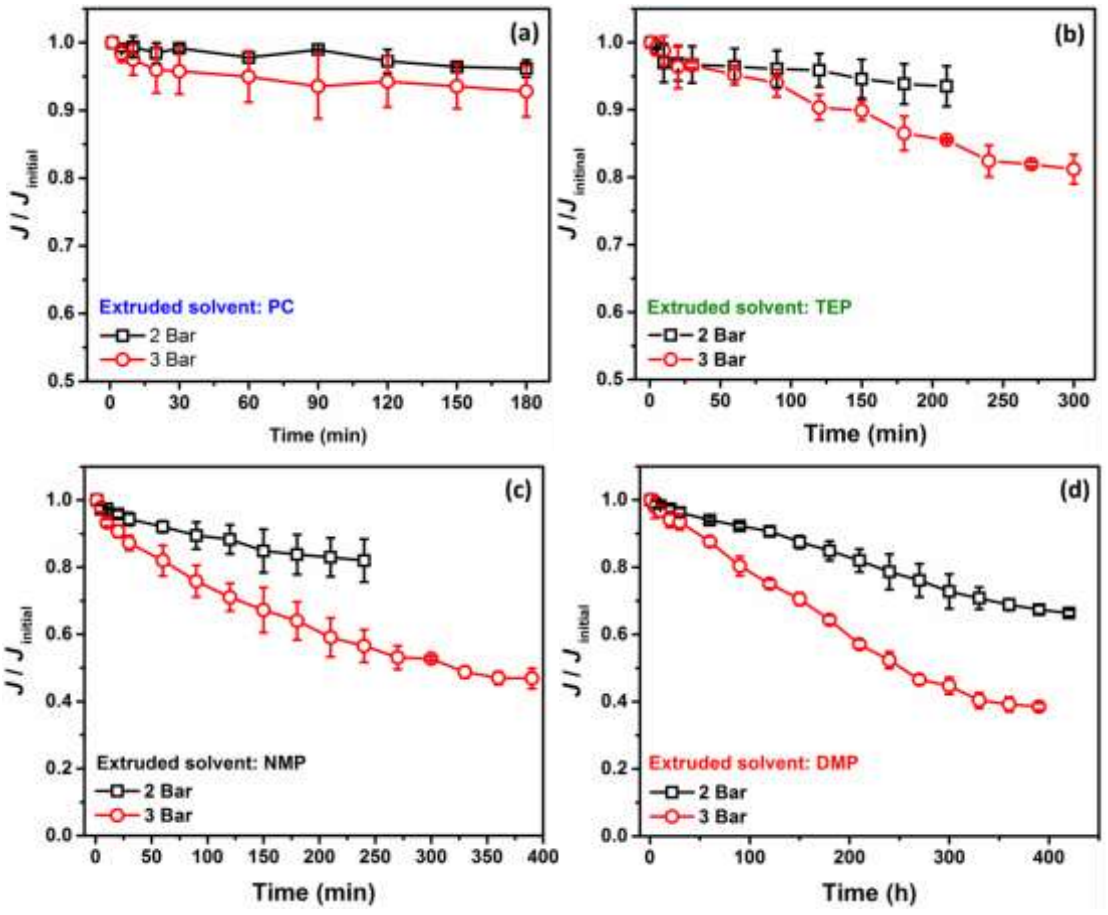

Fig. S3 Variation in the pure water permeabilities of PVDF hollow fiber membranes prepared with extruded PC (a), TEP (b), NMP (c) and DMP (d) during continuous pure water filtration at different operation pressure.

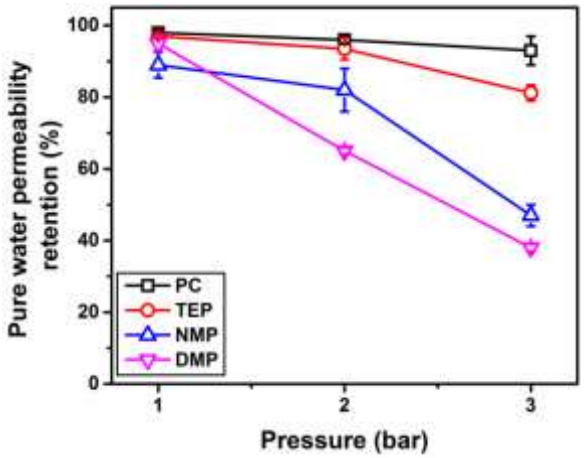

Fig. S4 The permeation stability of the membranes as a function of the operating pressure.

3. The relationship between the permeation stability and mechanical strength

The permeation stability and mechanical strength are significant parameters, both of which represent the compressive and tensile properties of a membrane, respectively. Hence, it is highly demanded to investigate the relationship between the permeation stability and mechanical strength of the membrane. The result is shown in Fig. S5. It is clear that the mechanical strength of the membranes changed slightly with the drastic increase in the permeation stability. As mentioned before, the permeation stability depends on the sub-layer of the membrane,[4-6] while the mechanical strength is determined by the bulk structure of the membrane. In this work, extruding solvents at the outer layer of the membranes only affected the surface and sub-layer structures of the membranes, rather than the bulk structure. Hence, the permeation stability of the membrane could be enhanced obviously, whereas the mechanical strength was hardly affected.

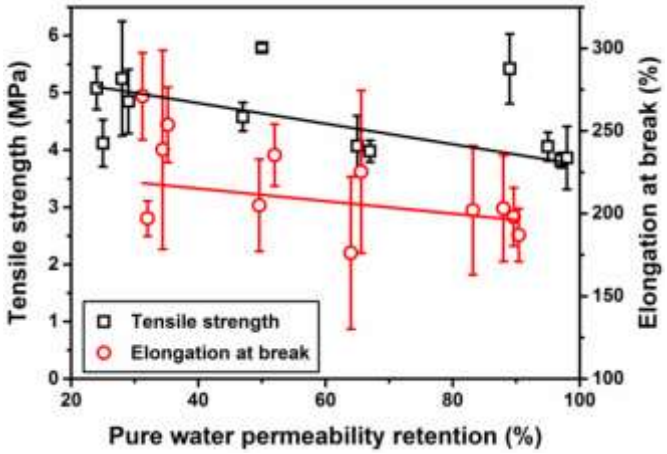

Fig. S5 The relationship between the mechanical strength and permeation stability of the PVDF membranes.