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High performance PVDF membranes prepared by the Combined Crystallisation and Diffusion (CCD) using a dual-casting technique: a breakthrough for water treatment applications

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Materials

Commercial PVDF (Kynar®K-761, MW = 440,000 Da, ρ = 1.79 g/cm3) was purchased from Elf Atochem. DMSO (HPLC grade), isobutanol (HPLC grade), n-hexane (GPR), and ethanol were purchased from VWR, UK. DMSO was used as a solvent for PVDF in preparing dope solutions. Isobutanol was used to prepare an isobutanol-water mixture for liquid-liquid porometry. Ethanol and n-hexane were used in solvent exchange steps before drying the membranes. The dried membranes were then used for SEM imaging.

Membrane Characterisation

Scanning Electron Microscope (SEM)

The morphology of the membranes prepared is observed using SEM (LEO Gemini 1525 FEGSEM, Tokyo, Japan). For sample preparation, wet membrane samples are first subjected to two cycles of ethanol immersion, followed by two cycles of n-hexane immersion, with each immersion cycle lasting a period of 4 hours. After immersion, the membranes are dried out and used for SEM. The membrane cross-section samples are prepared by fracturing the dried membranes in liquid nitrogen. The prepared samples are finally gold-coated at 10nm thickness to make the surface electrically conductive, ready for SEM observation

Liquid-Liquid Displacement Porometry

The pore sizes and the pore size distribution were measured using a liquid-liquid displacement porometer (LLP 1500A, Porous Materials Inc., USA). A mixture of 1:1 (v/v) isobutanol-water is prepared which separates into two equilibrated phases - an isobutanol rich phase and a water-rich phase. The membranes are pre-wet with isobutanol rich phase while the water-rich phase is used to push the wetting liquid out of the pores by application of pressure. At each step change in pressure, the permeate flux is measured. The pore sizes corresponding to the operating pressure is given by Young-Laplace equation:

$$d = \frac{4.\gamma.cos\theta}{\Delta p} \qquad \text{Equation 1}$$

where d is the pore diameter, γ is the interfacial tension between the two liquids (1.7 mN/m), θ is the contact angle of the wetting liquid on the membrane surface (taken as 0 ° due to complete spreading) and Δp is the pressure difference across the membrane.

Pure Water Permeance (PWP)

The PWPs of the membranes were characterised using a 1000ml dead-end filtration cell. Pure water was used as the feed liquid and the applied pressure difference was 1 bar. The permeance measurements were taken for a period of 20 mins and can be calculated using
the following formula:

$$PWP = \frac{J_w}{p} = \frac{V}{A \times \Delta t \times p} \qquad \text{Equation 2}$$

where PWP is the pure water permeance ($L.m^{-2}.hr^{-1}.bar^{-1}$ or $LMH.bar^{-1}$), J_w is the pure water flux ($L.m^{-2}.hr^{-1}$ or LMH), V is the permeated volume (litres) in time Δt (hours), A is the effective membrane area (m^2) and p is the applied pressure difference (bar). 5 sample measurements were performed from different membranes of each type and the average of these values was reported as the PWP.

Mechanical Strength

Mechanical properties of the membranes were tested according to a standard method described in the American Society for Testing and Materials (ASTM) D882 using a tensile testing machine, Lloyd EZ50. The width of the samples was fixed at 10mm and the gauge length at 50mm. The thickness of the samples was measured using a digital caliper. The samples were then stretched at a constant rate of 10mm/min, and the tensile force was recorded by a transducer. Different parameters such as load applied, elongation ratio, tensile stress and Young's modulus were recorded and measured. For each membrane type, 10 samples were tested and the average value was then reported.

Supplementary figures

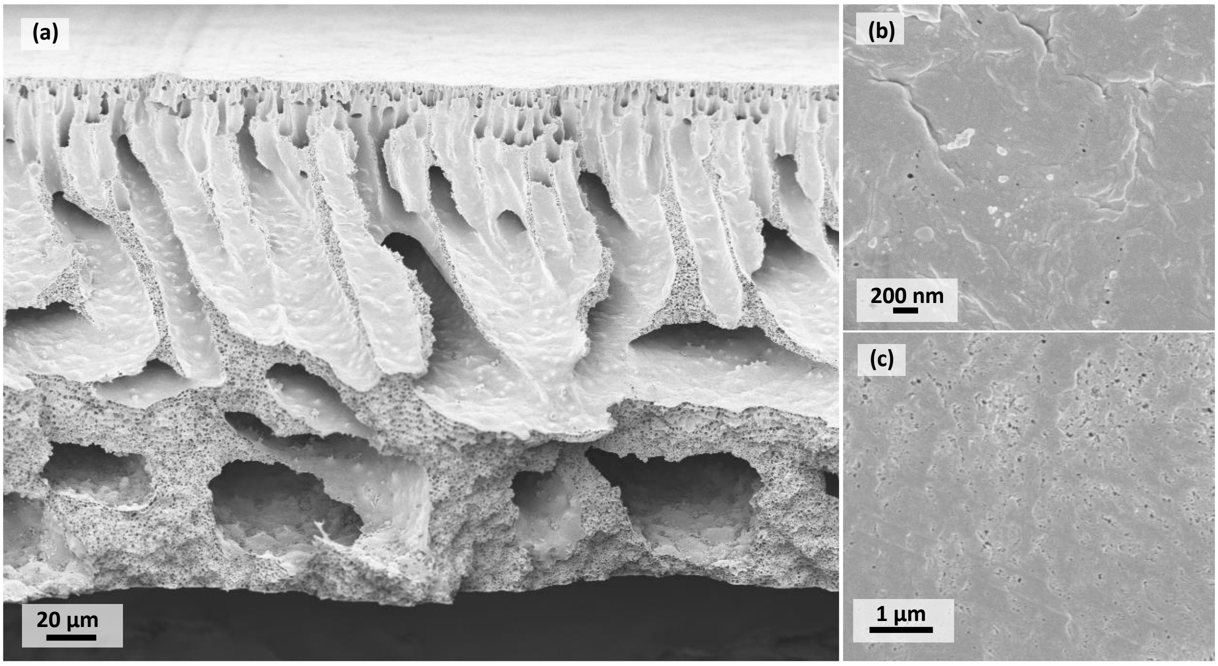

Figure S1. SEM images of 20PVDF_NIPS showing (a) cross-sectional overview; (b) top surface view; (c) bottom surface view

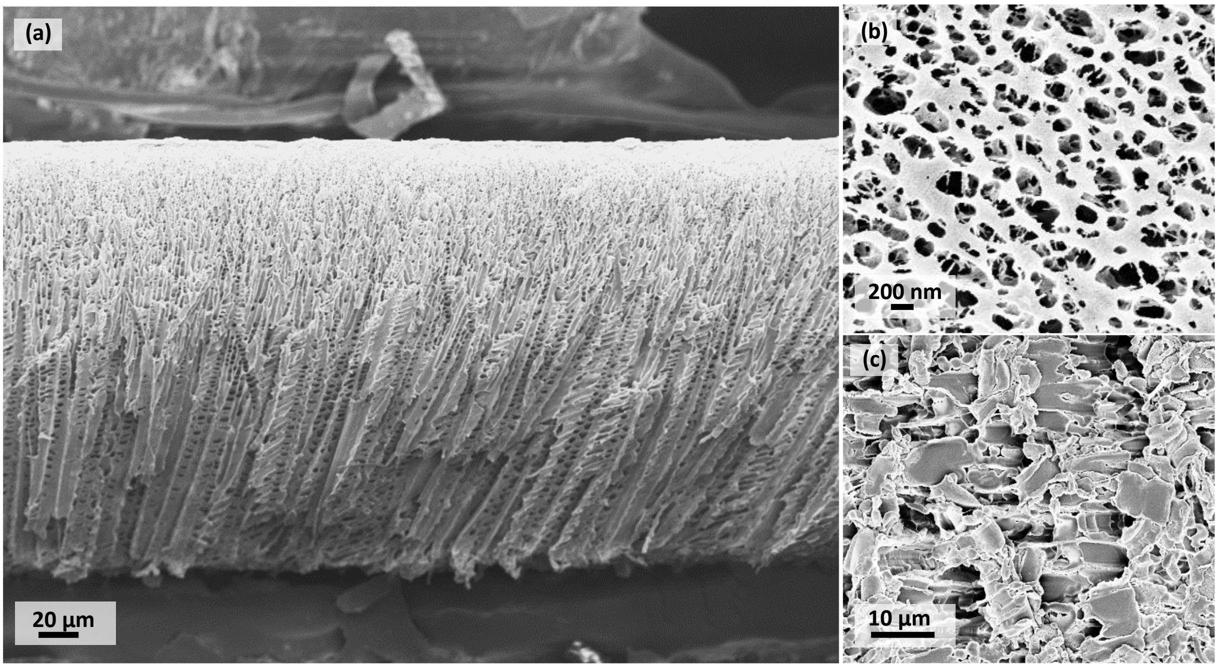

Figure S2. SEM images of 15PVDF_CCD showing (a) cross-sectional overview; (b) top surface view; (c) bottom surface view

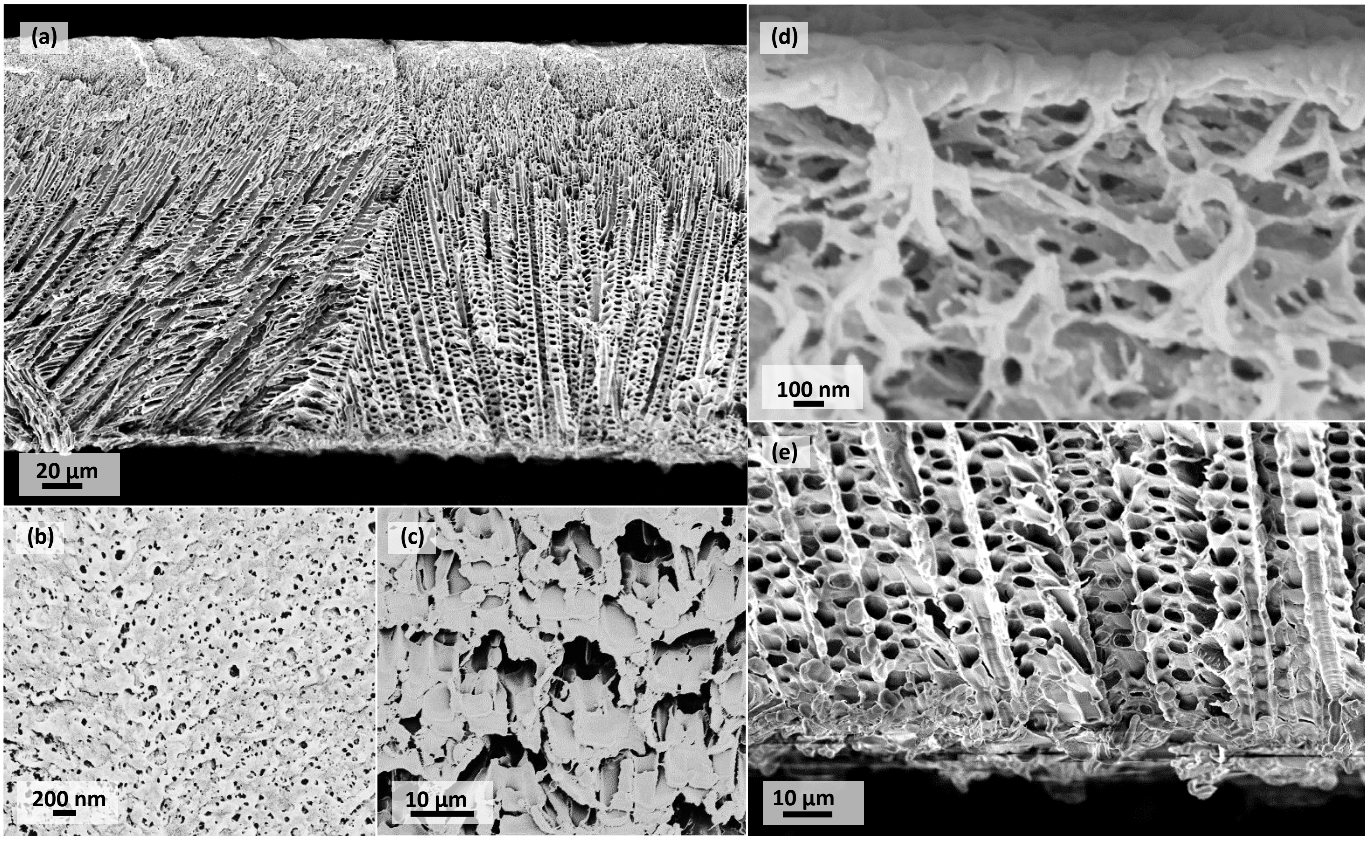

Figure S3. SEM images of 20PVDF_15PVDF_CCD showing (a) the cross-sectional overview; (b) top surface view; (c) bottom surface view; (d) cross-sectional view of the separation layer; (e) cross-sectional view of the microchannels found in the support layer

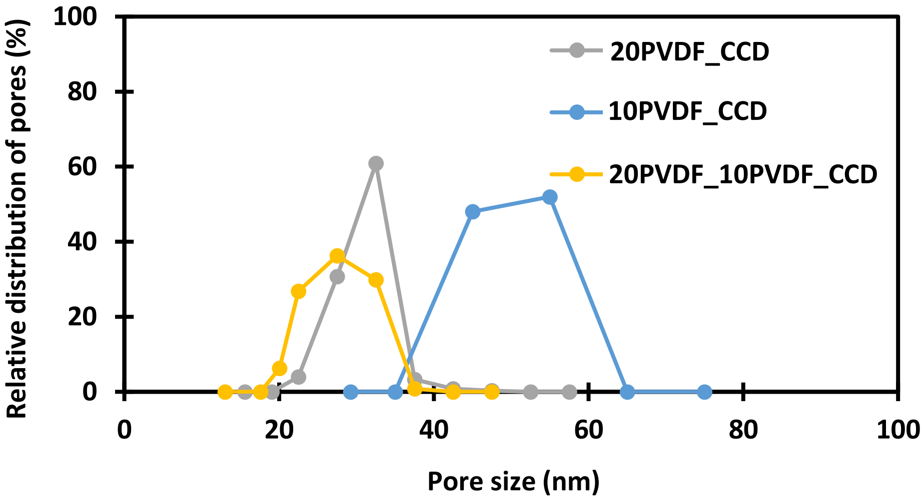

Figure S4. Pore size distribution comparison of 20PVDF_CCD, 10PVDF_CCD and 20PVDF_10PVDF_CCD

Supplementary Tables

Table S1. Compilation of pore sizes (nm) and pure water permeances (LMH.bar^{-1}) from various literature works on ultrafiltration PVDF membranes.

Modification	**Membrane**	**Pore size (nm)**	**PWP (LMH.bar^{-1})**	**Reference**
Pure PVDF membranes	PVDF with varying solvents	N/A but UF	68.76	[1]
	PVDF with mixed solvents	40	143	[2]
	PVDF with increased evaporation time (airgap)	69	152	[3]
	PVDF with ethanol as internal coagulant	88	155	[3]
Modified with small molecular additives	PVDF with small molecular additives	45	291	[4]
	PVDF with ethylene glycol as non-solvent additive	34.28	25.4	[5]
	PVDF with 1,2 ethanediol as non-solvent additive	36	49	[6]
Modified with polymeric additives	PVDF blend with PVP	44	309	[7]
	PVDF blend with PVA	47	259	[7]
	PVDF blend with PMMA	15-25	209	[8]
	PVDF blend with cellulose nanocrystals	31	207	[9]
Modified with inorganic additives	PVDF blend with LiCl.H_2O and TiO_2	34	82.5	[10]
	PVDF blend with TiO_2 nanoparticles	47	112	[11]
	PVDF blend with Al_2O_3 nanoparticles	20-50	200-225	[12]
	PVDF blend with SiO_2 sol	99	301	[13]
	PVDF blend with TiO_2 nanowire	44	266	[14]
	PVDF blend with graphene oxide	55	458	[15]
	PVDF blend with graphene oxide and PVP	N/A but UF	360	[16]
	PVDF blend with reduced graphene oxide and TiO_2 nanocomposites	76	77	[17]
	PVDF blend with graphene oxide	13	27	[18]
	PVDF blend with zinc oxide-graphene oxide composites	43	171	[19]
	PVDF blend with graphene oxide and TiO_2	65	488	[20]
	PVDF blend with Zinc-Iron oxides nanoparticles	29	224	[21]
	PVDF blend with graphene oxide-PEG nanocomposites	25.3	94	[22]
	PVDF blend with TiO2-HNTs nanocomposites	93.9	354	[23]
	PVDF blend with hydrothermal carbon nanospheres	58.3	950	[24]
	PVDF blend with Mg-Al nanolayered double hydroxide	55	351	[25]

	PVDF blend with PVP and graphene oxide nanoribbones	62.4	532	[26]
	PVDF blend with PVP-TiO_2-dopamine	64	243	[27]
	PVDF blend with nano-ZnO particles	31	147	[28]
	PVDF blend with TiO_2-activated carbon	31	225	[29]
	PVDF blend with Fe_3O_4-palygorskite nanocomposites	21	356	[30]
	PVDF blend with Mg-Al LDH nanoparticles	32	106.5	[31]
	Hydroxyl functionalized PVDF-TiO_2	60	50	[32]
	PVDDF blend with grapheneoxide-TiO_2 nanocomposites	78.4	75	[33]
	PVDF with modified with polydopamine polymerisation and ammonium fluotitanate hydrolysis	N/A but UF	228	[34]
Modified with graft/block copolymers	PVDF blend with PFSA-g-graphene oxide	77	587	[35]
	PVDF blend with sulfonated poly(α,β,β-trifluorostyrene)	40-50	103	[36]
	PVDF blend with poly(aminoanthraquinone)/reduced graphene oxide	11	70	[37]
	PVDF modified with self-doped sulfonated polyaniline	N/A but UF	160	[38]
	PVDF blend with PMMA-b-PSBMA	30	188	[39]
	PVDF blend with PVP-g-MMT nanocomposites	16	75	[40]
	PVDF blend with SiO_2-g-PDMS nanoparticles	16	115	[41]
	PVDF blend with PVDF-g-PMEMA	58.4	77	[42]
	PVDF-blend with PVDF-g-PEGMA	73	7779	[43]
	PVDF-blend with PVDF-g-PEGMA	31	5170	[44]
Other methods	PVDF with graphene oxide-water as coagulation bath	91	460	[45]
	Electrospun PVDF nanofibers with top chitosan layer	N/A but UF	205	[46]

Note: Many studies characterise pore sizes in many different ways and do not follow a standardised method. Therefore, these values should be used for reference purposes only to get an approximate idea of the membrane's separation capabilities. Also the reporting of pure water permeances varies significantly across various studies. For some studies the pure water flux (L.m^{-2}.hr^{-1} or LMH) values were read off from the figures and so would only be approximate values. These values have been converted using the operating conditions mentioned in the respective studies to units of permeances which is LMH.bar^{-1} (L.m^{-2}.hr^{-1}.bar^{-1}) to allow for fair comparison. Moreover, Table 1S is not an exhaustive list of all PVDF membrane related studies. Many studies work on PVDF microfiltration membranes and these have not been included in the Table 1S. Many studies that do focus on PVDF-UF membranes, either do not characterise the pore sizes or have gas permeability data instead of water permeability. Again these studies are not covered here.

Table 2S. Pure water permeances (PWPs) and corresponding pore sizes of PVDF membranes produced commercially by industry leaders[a]

Supplier	Membrane Brand	Pore size (nm)	Operating conditions from data sheets [b,c,d]	PWP[e] (LMH.bar^{-1})	Ref.
Dow-Dupont	IntegraPac	30	Filtrate Flux = 40-90 L.m^{-2}.hr^{-1} Max TMP = 2.1 bar	40-90	[47]
	IntegraFlux	30	Filtrate Flux = 40-110 L.m^{-2}.hr^{-1} Max TMP = 2.1 bar	40-110	[48]
Suez	ZeeWeed 1000	20	Flow range = 55-110 m^3.day^{-1} Membrane area = 41.8-51.1 m^2 TMP range = 0-0.9 bar	61-122	[49]
	ZeeWeed 1500	20	Flow range = 45-180 m^3.day^{-1} Membrane area = 55.7 m^2 TMP range = 0-2.76 bar	34-135	[50]
Hydranautics	HYDRAcap MAX	80	Filtrate Flux = 34-110 L.m^{-2}.hr^{-1} Max TMP = 2 bar	34-110	[51]
KOCH	PURON	30	Typical Production range = 2-6.8 m^3.hr^{-1} Membrane area = 51 m^2 Max TMP = 1.7 bar	40-133	[52]
QUA	EnviQ	40	Filtrate Flux = 10-25 L.m^{-2}.hr^{-1} TMP range = 2 psi-4 psi	72-180	[53]
TORAY	MEMBRAY	80	Design Flow = 8-53 m^3.day^{-1} Membrane area = 70 m^2 TMP = 0.2 bar	24-158	[54]

[a] The pure water permeances and pore sizes were obtained from specification data sheets published by the supplier. These data sheets were obtained from their respective websites.

[b] Different data sheets present filtration specifications in different ways. For some data sheets use the terms such as “Flow range”, “Production range” or “Design flow” instead of “Filtration flux” or “Permeation flux”. This value is assumed to be the permeate flow range and not the feed flow range in our calculation. This is because if it were to be the feed flow range, the permeate flow would be even lower.

[c] A conservative estimate of the transmembrane pressure is taken to maximise the value computed for the Flux. For many products, the operating pressure was not mentioned, but instead the Max TMP (transmembrane pressure) was mentioned. In these cases if the Max TMP was above 1 bar, then for the flux calculation, the operating pressure was taken as 1 bar and not the Max TMP. This gives a higher value for the Flux.

[d] For Zeeweed 1000, the data sheets provides an approximate range of the membrane area. In this case again, a lower value of the membrane area is taken for the calculation of flux.

[e] PWP (LMH.bar^{-1}) = Filtration rate [L.hr^{-1}] / (Membrane area [m^2] x TMP [bar])
= Filtrate Flux [L.m^{-2}.hr^{-1}]/TMP [bar]

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