Supplementary Information for the manuscript

Title

2D nanosheet enabled thin film nanocomposite membranes for freshwater production – a review

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Table S1 2D-enabled TFN RO membranes with data on 2D nanosheets, membrane surface and performance.

Entry	Nanosheet type and production method	Average size (S) and thickness (T)	Optimum concentration in (x) phase	Substrate membrane	Impact on membrane surface parameters (R - roughness, PAT - PA layer thickness, CA - contact angle, ZP - zeta potential at pH 7, ↑ - increases, ↓ - decreases	Membrane surface parameters	Pure water permeance of control membrane (LMH/bar)	Pure water permeance of TFN membrane (LMH/bar)	Performance enhancement (%)	NaCl rejection (%)	TFN membrane performance	Ref.
1	GO, Hummers method	S = 70 – 140 nm	0.0038 wt% (A)	PSf	R ↓, PAT ↓, CA↓, (-ve) ZP ↑	R = 67 nm (average), ZP = -41.5 mV, CA= 49°, PAT = 248 nm	0.59	1.07	81.36	99.28 → 99.40	• Biovolume of cells attached on the membrane decreased by approximately 98% compared to control membrane. • Negligible difference in water permeance and salt rejection after chlorine exposure while control membrane reported 3 times increase in flux and 9% drop in salt rejection.	[1]
2	GO, modified Hummers method		0.01 wt% (A)	PSf	R ↑, PAT ↓, CA ↓	CA = 56°, PAT = 1.93 µm	1.42	1.97	38.73	98.5 → 98	• After multiple fouling-cleaning cycles the flux recovery of TFN membrane was 85 % when compared to 50 % for control and commercial membrane. • After 500 ppm NaOCl chlorination for 10 hr significant increase of 20% in water flux was observed and the salt rejection decrease was negligible when compared to control membranes.	[2]
3	GO, Hummers method	S = 360 nm, T = 2 nm	0.12 wt% (A)	PSf	PAT ↑, CA ↓, (-ve) ZP ↑		0.122	0.219	79.51	97.54 → 86	• Higher cytotoxicity of the membranes with cell viability percentage of approximately 33% when compared to pristine membrane with 87%.	[3]
4	GO, modified Hummers method	S = 500 nm – 2 µm	0.015 wt% (O)	PSf	R ↓, CA ↓	R = 120 nm (RMS), CA = 58°, PAT = 200-300 nm	1.88	2.87	52.66	95.7 → 93.8	• Stable water permeance and salt rejection during 72 h long term filtration experiments.	[4]

5	GO, Staudenmaier method		0.0053 wt% (O)	PSf	R ↓, CA↓, (-ve) ZP ↑	R = 52 nm (RMS), ZP = -16 mV, CA = 68°	1.7	2.3	35.29	96 → 96	• Adsorption of organic matter on the membrane surface was significantly reduced. • Cell viability rate decreased to 52% when compared to control membrane with 85%.	5
6	mGO, modified Hummers method and functionalisation		0.003 wt% (A)	PSf	R ↓, PAT ↓, CA ↓	R = 67.4 nm (RMS), CA = 48.2°, PAT = 50-80 nm	1.26	1.57	24.60	99.5 → 99.7	• Exhibits bacterial killing ratios of 95.4% and 83.4% against E. coli and S. aureus which is much higher than 4.95 % and 2.48% of control membrane.	6
7	Ag-GO		0.008 wt% (A)	PSf	R ↓, CA↓, (-ve) ZP ↓	R = 42 nm (average), ZP = -28 mV, CA = 35°	1.47	1.35	-8.16	96.7 → 94.8	• Decrease in both permeance and salt rejection. • FRR increased from 36.36% to 89.27% and irreversible fouling decreased from 62.62% to 10.72% respectively when compared to control membrane. • 85.6% reduction of live E coli cells after 1 h compared to 5.4% of control membrane.	7
8	g-C_3N_4, Thermal decomposition	S = 60 – 70 nm	0.015 wt% (A)	PSf	R ↓, CA↓	R = 18 nm (average), CA = 63.3°	3	3	0.00	99 → 99.7	• No significant improvement in anti-fouling and permeance performance	8
9	aCN, Thermal decomposition and functionalisation	S = 400nm	0.005 wt/v% (A)	PSf	R ↓, CA↓, (-ve) ZP ↓	R = 57.1 nm (RMS), ZP = -16 mV, CA = 40°	1.57	2.81	78.98	98.8 → 98.7	• After 21 h fouling experiments with BSA and HA separately, the total fouling rate was 34.7% and 30.1% respectively when compared to 47.5% and 41% for the control membrane. • FRR after BSA and HA fouling was 86.2% and 89.3% when compared to control membrane with 71.3% and 68%.	9
10	COOH-g-C_3N_4, Thermal decomposition and functionalisation		0.05 wt% (A)	PSf	R ↓, CA ↓, (-ve) ZP ↓	R = 4.1 nm (RMS), CA = 58.5°, PAT = 250 - 300 nm	3.96	6.12	54.55	96 → 98.1	• The normalised flux after 120 min filtration with 100 ppm BSA was maintained at 1.5 times that of g-C_3N_4 incorporated membranes.	10
11	g- C_3N_4, Thermal decomposition	S = 197 nm	0.01 wt/v% (A)	PSf	R ↑, PAT ↑, CA ↑, (-ve) ZP ↑	R = 173 nm (RMS), CA = 92.1°, PAT =	1.06	1.38	30.19	98.56 → 99.23	• After exposure to 200 ppm BSA, the total fouling rate	11

						80 nm					decreased to 18.3% when compared to control membrane at 31.2%.	
12	$BN(NH_2)$, Ball milling	S = 60 – 120 nm, T = 1.5 – 2.5 nm	0.02 wt% (A)	PES	R ↑, PAT ↓, CA ↑, (-ve) ZP ↑	R = 110.9 nm (RMS), CA = 42°, PAT = 229.33 nm	3.19	4	25.39	96 → 96.4	• HA fouling experiments demonstrated high flux recovery over 96% after one fouling/cleaning cycle when compared to 92% of the control membrane. • After 24 h exposure to 2000 ppm NaOCl, the salt rejection was observed to be lowered by 2% when compared to control membrane at 6%.	[12]
13	MoS_2, Liquid exfoliation	S = 100 – 600 nm, T = 2 nm	0.01% (O)	PSf	R ↑, PAT ↓, CA ↑, (-ve) ZP ↑	R = 80.6 nm (average), CA = 71°, PAT = 179 nm	5.07	6.2	22.29	98 → 99	• Fouling experiments demonstrated that 91% of the normalized water flux was retained for 100 ppm BSA after 14 h testing when compared to 86% for the control membrane. • Leaching of nanosheets during operation.	[13]
14	$Ti_3C_2T_x$, Acid etching	S = 200 – 800 nm, T = 3.5 nm	0.015 wt% (A)	PSf	R ↓, CA ↑, PAT ↓	R = 90 nm (RMS)	1.7	2.53	48.82	98.6 → 98.5	• After 6 h experimentations with 60 ppm BSA, the flux decline value was 11.1% when compared to control membrane with 22.72%. • After chlorination tests, the salt rejection remained above 97% while control membranes rejection decreased to 94%.	[14]
15	TpPa, Microwave synthetic technique	S = 40 – 60 nm, T = 5 nm	50 μg cm^{-2} (A)	PSf	R ↓, CA ↑, PAT ↓	R = 75.5 nm (RMS), ZP = -13.50 mV, PAT = 230 nm	0.7	2.2	214.29	96.3 → 97.7	• Salt rejection retained over 95% after chlorine exposure experiments. • High antimicrobial efficiency of 99.8% against E. Coli by surface contact inhibition.	[15]

Table S2 2D-enabled TFN NF membranes with data on 2D nanosheets, membrane surface and performance.

Entry	Nanosheet type and production method	Average size (S) and thickness (T)	Optimum concentration in (x) phase	Substrate membrane	Impact on membrane surface parameters (R - roughness, PAT - PA layer thickness, CA - contact angle, ZP - zeta potential at pH 7, ↑ - increases, ↓ - decreases)	Membrane surface parameters	Pure water permeance of control membrane (LMH/bar)	Pure water permeance of TFN membrane (LMH/bar)	Performance enhancement (%)	Na_2SO_4 rejection (%)	TFN membrane performance	Ref.
1	GO, modified Hummers method		0.2 wt% (A)	PSf	R ↓, CA ↓, (-ve) ZP ↑	R = 34.42 nm (RMS), ZP = -26 mV, CA = 65 °, PAT = 50 – 200 nm	0.12	1.48	1133.33	97 → 96	• Higher normalized flux observed during filtration studies with 200 mg/L BSA and 200 mg/L HA with 20 ppm when compared to control membrane. BSA cycle: Control = 68% TFN = 95% HA cycle: Control = 44% TFN = 90%	[16]
2	SGO, modified Hummers method and functionalisation		0.3 wt% (A)	PSf	R ↓, CA ↓, (-ve) ZP ↑	R = 23.48 nm (RMS), ZP = -23.48 mV, CA = 39.12°, PAT = 113.8 nm	1.27	2.37	87.3	96.62 → 96.45	• Fouling test with BSA and HA revealed enhanced performance towards BSA while deterioration for HA. Normalized flux reduced to 40% compared to control membrane at 46% for HA fouling. BSA fouling resulted in normalized flux at 70% compared to 38% for control membrane. • Acid-base cleaning resulted in negligible flux reduction at 2% and similar salt rejection.	[17]
3	GO-TETA, Hummers method and functionalisation		0.03 wt% (A)	PES	R ↓, CA ↓, ZP ↑	R = 3.2 nm (average), ZP = 5.1 mV, CA = 8.5°, PAT = 157 nm	8.3	12.2	46.99	46.3 → 65.3	• Very low salt rejection. • FRR after fouling experiments with BSA achieved 95.3% compared to 89.3% for control membrane.	[18]
4	GO-EDA,		0.006	PSf	R ↓, CA ↓, ZP ↑,	R = 42.7 nm,	7.72	11.92	54.40	99 → 98.2	• Antifouling performance	[19]

	modified Brodie method		wt% (A)		PAT ↓	ZP = 25.5 mV, CA = 15°, PAT = 75.9 nm					• improved at pH = 3, however no notable difference was observed at pH= 6 compared to control membrane. • Post chlorine exposure salt rejection decreased to 88% compared to 86% for control membrane.	
5	GO-PEI, modified Brodie method		0.004 wt% (A)	PSf	R ↓, CA ↓, ZP ↑, PAT ↓	R = 60.9 nm (average), ZP = 41.2 mV, CA = 16°, PAT = 62.5 nm	7.72	12.42	60.88	99 → 98.2	• Antifouling performance improved at pH = 3, however no notable difference was observed at pH = 6 compared to control membrane. • Post chlorine exposure salt rejection decreased to 96% compared to 86% for control membrane.	19
6	MAH-GO, modified Hummers method and functionalisation	S = 400 – 800 nm, T = 1.3 nm	0.006 wt% (A)	PSf	R ↓, CA ↓, (-ve) ZP ↑, PAT ↓	R = 5.43 nm (average), ZP = -33 mV	4.67	8.22	76.7	98 → 97.6%	• Higher normalized flux observed during filtration studies with BSA. • Enhanced resistance to chlorine exposure.	20
7	g-C_3N_4, Thermal oxidation		0.0025 wt% (A)	PSf	R ↓, CA ↓, (-ve) ZP ↑	R = 35.2 nm (RMS), ZP = -35 mV, CA = 24.6°	10.45	18.8	79.90	90 → 84	• Normalized flux value was nearly twice that of the control membrane after 30 h fouling experiment with BSA. • Normalized fluxvalue was maintained approximatelyat 85% when compared to control membrane with 76% after 30 h filtration experiment with HA.	21
8	g-C_3N_4	S = 200 nm	16.4 µg cm^{-2} (A)	PSf	R ↑, PAT ↑, CA ↓	R = 39 nm (RMS), ZP = -20 mV	11	20.5	86.36	98.6 → 94.5	• High membrane stability after 8 h continuous filtration process.	22
9	$BN(NH_2)$, Ball milling	S = 100 nm, T = 1.5 nm	0.004 wt% (A)	PES	R ↑, PAT ↓, CA↓, (-ve) ZP ↑	R = 21.4 nm (average), ZP = - 6.30 mV, CA = 30°	12.92	13.88	7.43	68.93	• 97% normalized flux after filtration experimentation for 6 h with HA	23
10	$BN(NH_2)$, Ball milling	S = 100 – 200 nm, T = 5 nm	0.003 wt% studded	PES	R ↓, CA↓, (-ve) ZP ↑	R = 6.13 (RMS), ZP = -34.85 mV, CA	4.81	7.65	59.04	88.3	• Exhibited 59% enhancement in flux and 50% improvement in total fouling resistance when	24

			on PA layer			= 25°, PAT = 53.56 nm					compared to control membranes and maintained NOM separation well above 90%.	
11	$BN(NH_2)$, Ball milling	S = 100 – 200 nm, T = 1.5 – 5 nm	0.003 wt% (A) + 0.003 wt% studded on PA layer	PES	R ↑, CA↓, (-ve) ZP ↑	R = 12 nm (RMS), ZP = -70 mV, CA = 20°	7.2	12.15	68.75		• Normalized flux of 95% after 6 h fouling experimentation which was higher than control membrane. • NOM removal from surface water in terms of UV245 and DOC at 650% and 341% more than treatment plant. • Better filtration performance in detrimental solution chemistry of low pH and high Ca^{2+} concentrations.	[25]
12	MoS_2, Liquid exfoliation	S = 200 – 600 nm, T = 3 nm	0.01 wt/v% (O)	PSf	R ↑, CA↓, (-ve) ZP ↑	R = 30.4 nm (RMS), ZP = -32.8 mV, CA = 64°	3.4	7.8	129.41	92.5 → 94.4	• After 16 h experimentation with saline solution, the flux reduction was 6.9% when compared to 25.6%decline in control membrane.	[26]
13	TA-MoS_2, Liquid exfoliation	S = 37.41 nm, T = 1.35 nm	0.025 wt% (A)	PES	R ↑, CA↓, (-ve) ZP ↑	R = 100.9 nm (RMS), ZP = -70 mV, PAT = 32 nm	13.67	17	24.36	97 → 98.5	• Normalized flux after 4 h experimentation with BSA was very similar to that of the control membrane in the range 55% to 60%. • High flux and salt rejection above 98% retained after 120 h experimentation with saline solution.	[27]
14	TA-Fe^{3+}-MoS_2, Liquid exfoliation	S = 500 – 1500 nm, T = 5 – 6 nm	0.01 wt% (A)	PSf	R ↑, CA ↑, PAT ↓	R = 26.7 nm (RMS), CA = 38.5°, PAT = 75 nm	4.9	7.6	55.10	95.6 → 96.3	• Increased salt rejection and permeance when compared to control membranes.	[28]
15	O-MoS_2, Hummers method	S = 100 – 500 nm, T = 1.8 – 5 nm	0.01 wt/v% (O)	PSf	R ↑, CA↓, (-ve) ZP ↑	R = 26.5 nm (RMS), ZP = -35 mV, CA = 41°	3.11	7.91	154.34	93.4 → 97.9	• After 90 min experimentations with 500 mg/L BSA, the membranes exhibited normalized flux of 78%, while the control membrane exhibited 57%.	[29]
16	TpBD-NH_2, Liquid exfoliation	S <10 µm, T = 4 nm	0.01 wt/v% (A)	PAN	R ↑	R = 21.7 nm (RMS), CA = 35°	4.8	9.5	97.92	98 → 92	• Water permeance boosted but the selectivity decreased.	[30]

Table S3 Comparison of 2D enabled TFN membranes and challenges associated

2D nanosheet material	2D nanosheet production aspects	Characteristics of 2D enabled TFN membranes	Challenges of 2D enabled TFN membranes	Ref.
GO	• Scalable and high yield synthesis methods. • Cheap and abundant available parent materials. • Production of hazardous gas and wastewater during synthesis	• Hydrophilicity • Negative charge • Antibacterial and organic fouling resistance • Chlorine resistance	• Low stability of GO in aqueous media and higher temperature. • Trade-off between permeance and selectivity. • Lower impact as permeance and selectivity enhancers.	5, 27
$g\text{-}C_3N_4$	• Lower dispersion and stability in solvents • Time consuming and low efficiency of nanosheet production.	• Hydrophilicity • Positive charge • Chlorine resistance • Permeance enhancer	• Trade-off between permeance and selectivity. • Low compatibility with polymer matrix	11, 21
BN	• High cost of BN. • High efficiency and scalable production method.	• Hydrophilicity • Negative charge • Mechanical strength • Chlorine resistance	• Trade-off between permeance and selectivity • Low permeance enhancement • Impact of amine functionalities overpowering BN.	12, 23, 24
MoS_2	• High cost of MoS_2 • Use of hazardous solvents and time-consuming methods. • Compatibility and stability issues.	• Hydrophilicity • Negative charge • Permeance enhancer • High selectivity retained	• Leaching of nanosheets due to poor compatibility and lack of functional groups. • The performance of membranes varies accordingly when different functional groups are attached to 2D nanosheets.	13, 27, 28
MXene	• Complex and costly synthesis methods. • Use of strong and corrosive chemicals.	• Hydrophilicity • Negative charge • Chlorine resistance • Permeance enhancer • High selectivity retained.	• Compatibility of nanosheets with polymer matrix. • Stability issues when in contact with water. • Possible leaching during operation.	14, 31
COF	• High cost, complicated and time-consuming synthesis. • Limited characterization data available	• Hydrophilicity • Negative charge • Permeance enhancer • Chlorine resistance • Antibacterial resistance. • High selectivity retained.	• Difficult to fabricate defect-free membrane. • Large size of nanosheets disrupts the PA layer formation.	15

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