Centre for Advanced Separations Engineering

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Fouling Resistant 2D Boron Nitride Nanosheet – PES Nanofiltration Membranes

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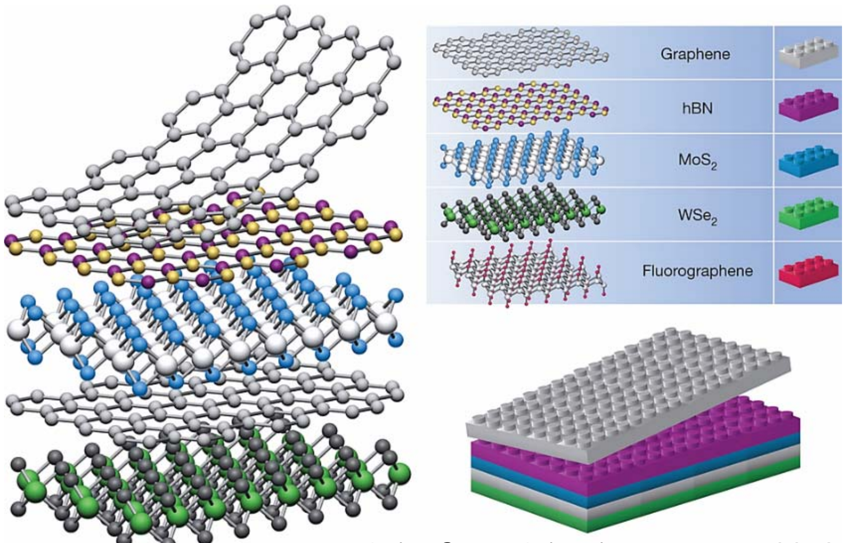
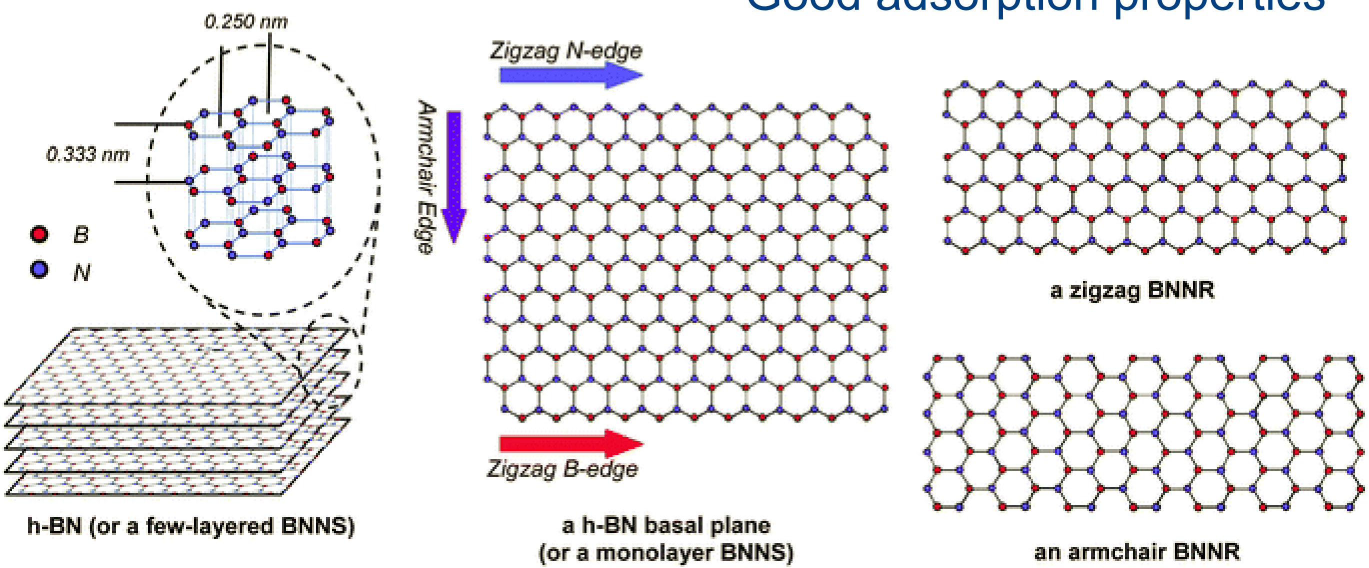
Boron Nitride Nanosheets (BNNS)



A. K. Geim & I.V. Grigorieva, *Nature*, **2013**

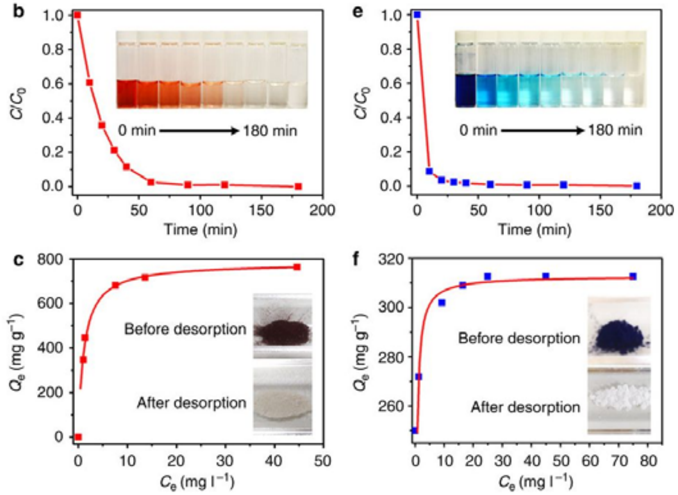
- 2D structure of hexagonal BN
- Isoelectric and isostructural analogue of graphene
- Strong covalent B-N bonds but with **ionic characteristics**
- High chemical and oxidation resistance
- High thermal conductivity and stability
- Good adsorption properties



Y. Lin & J. W. Connell, *Nanoscale*, **2012**

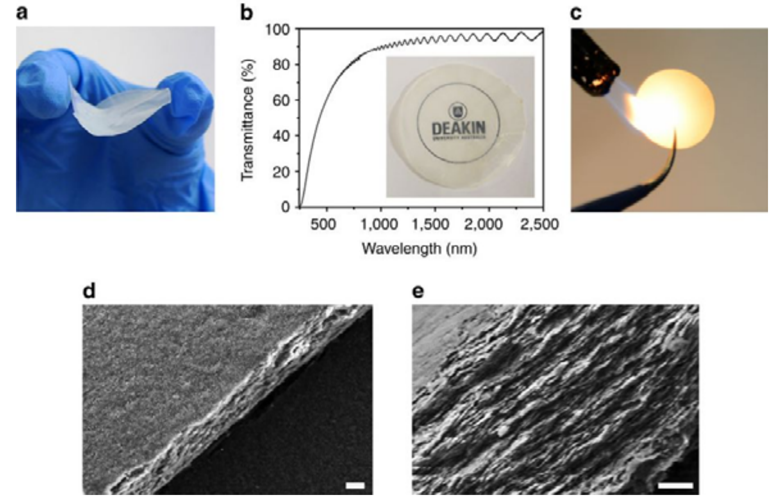
BNNS Sorbents and Membranes

BNNS sorbents for pollutant removal



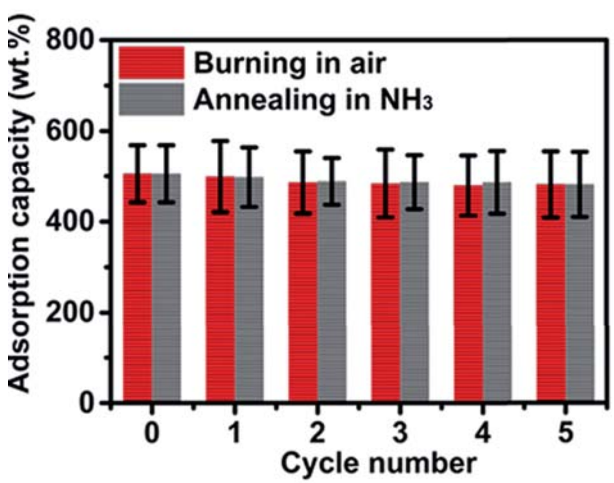
W. Lei et al., *Nature Comm.*, **2013**

BNNS aerogel



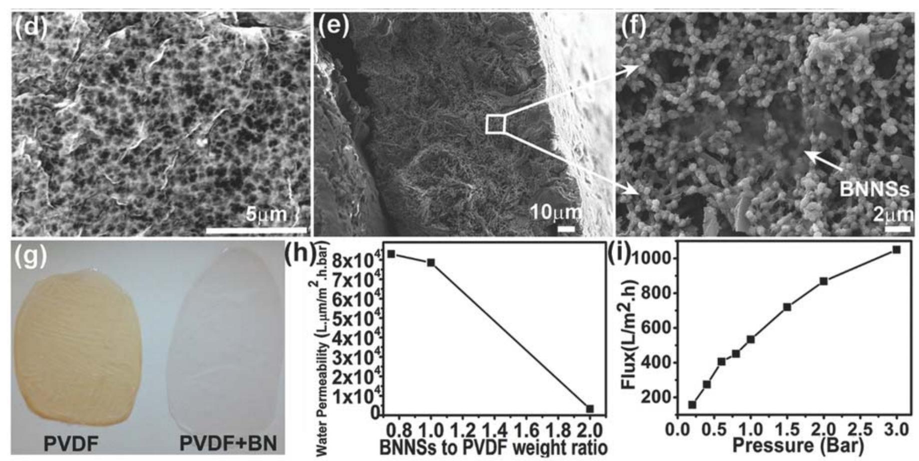
W. Lei et al., *Nature Comm.*, **2015**

BNNS monolith sorbent



Y. Xue et al., *J. Mater. Chem. A*, **2016**

Mixed-matrix PVDF-BNNS for oil removal



Y. Yu et al., *Adv. Mater. Interfaces*, **2015**
D. Liu et al., *Adv. Mater. Interfaces*, **2015**

Current Exfoliation Methods

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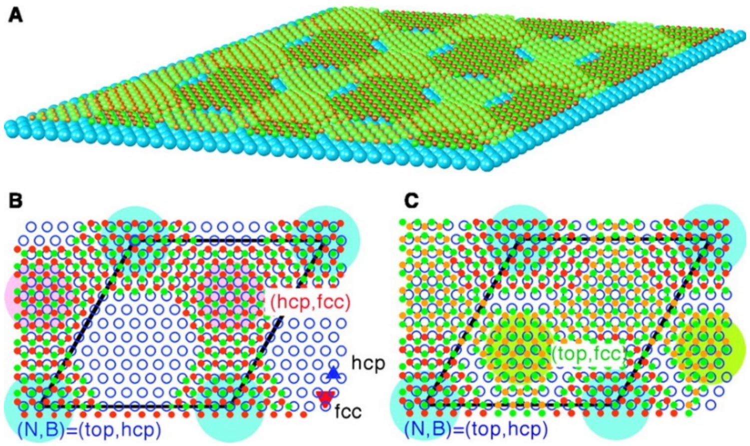
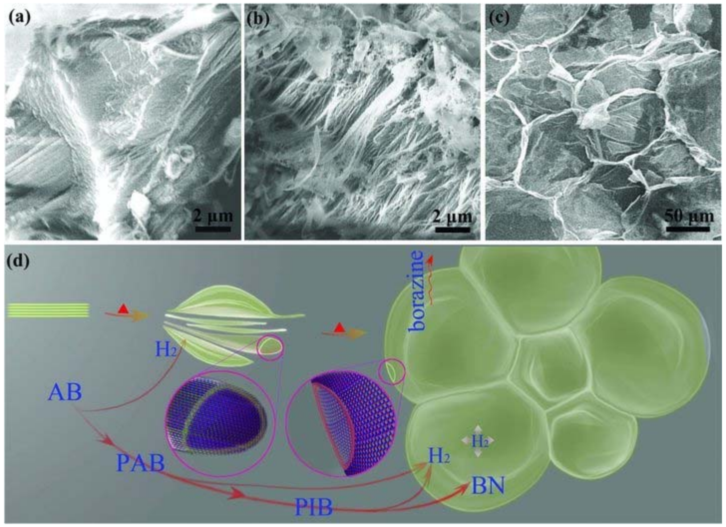
Thermal decomposition



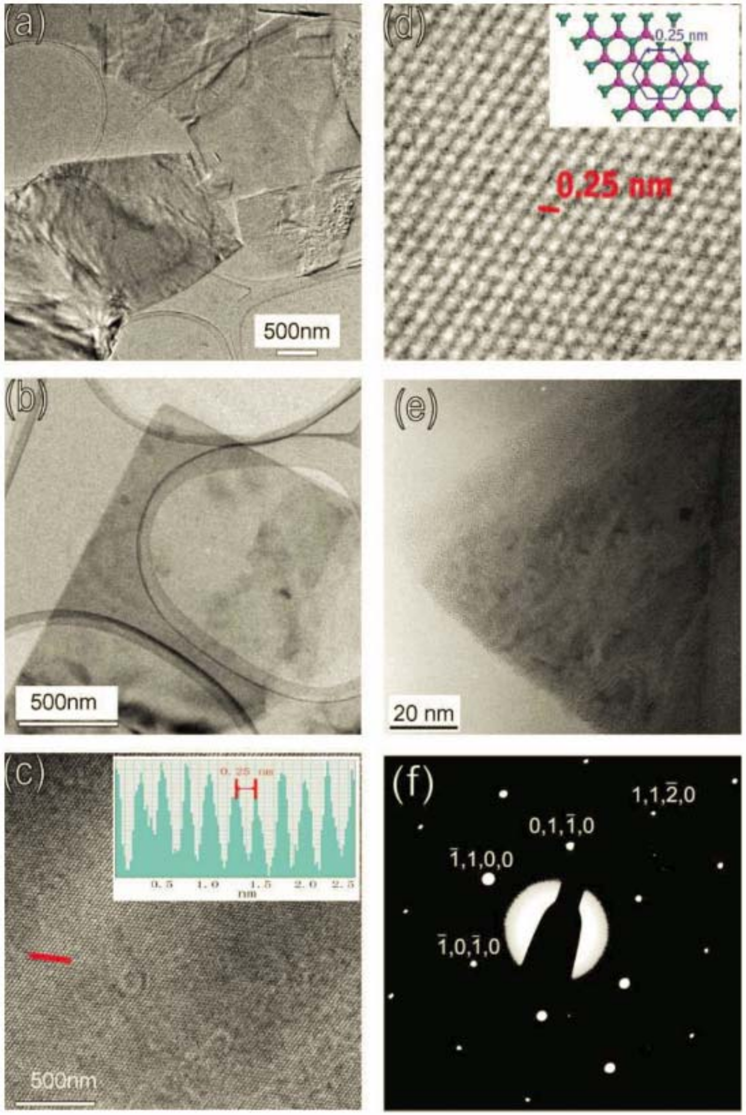
M. Corso et al., *Science*, **2004**

Chemical blowing



X. Wang et al., *Adv. Mater.*, **2011**

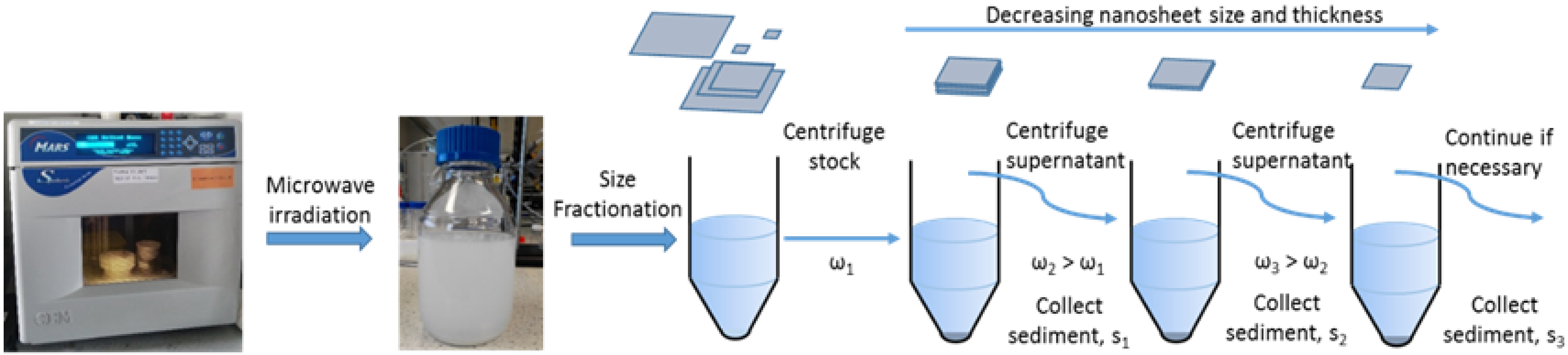
Exfoliation

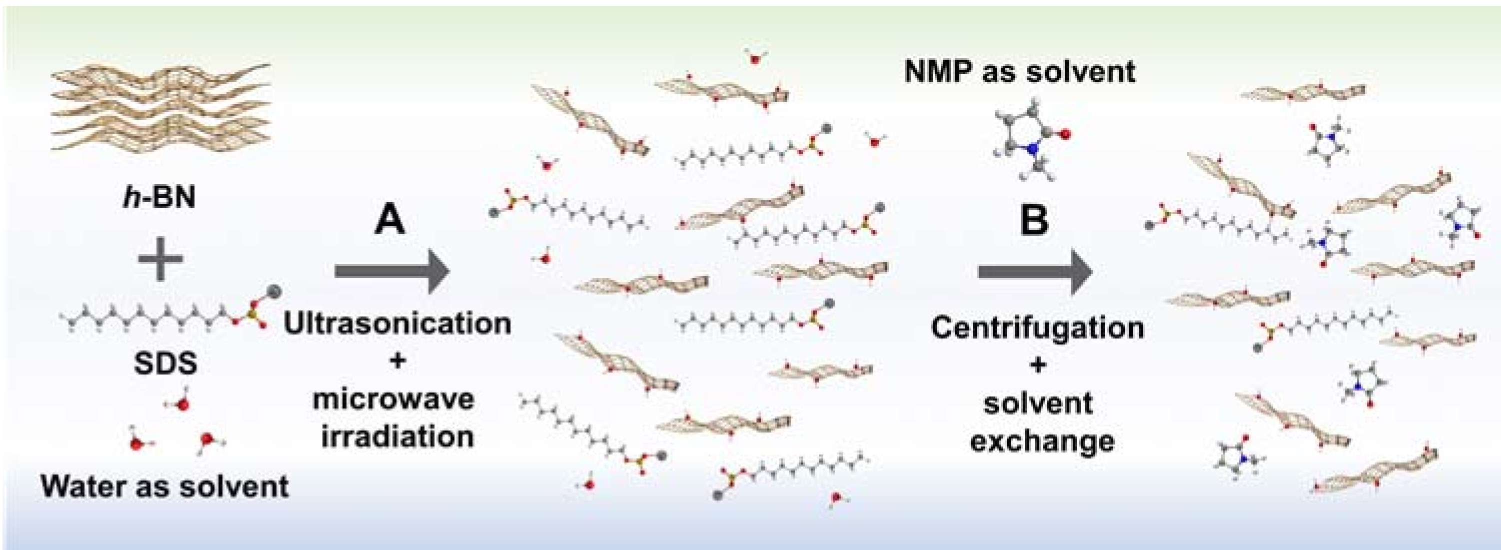


C. Zhi et al., *Adv. Mater.*, **2009**

Exfoliation of BNNS

❖ Exfoliation of *h*-BN (Step A) and preparation for its use as fillers (Step B)

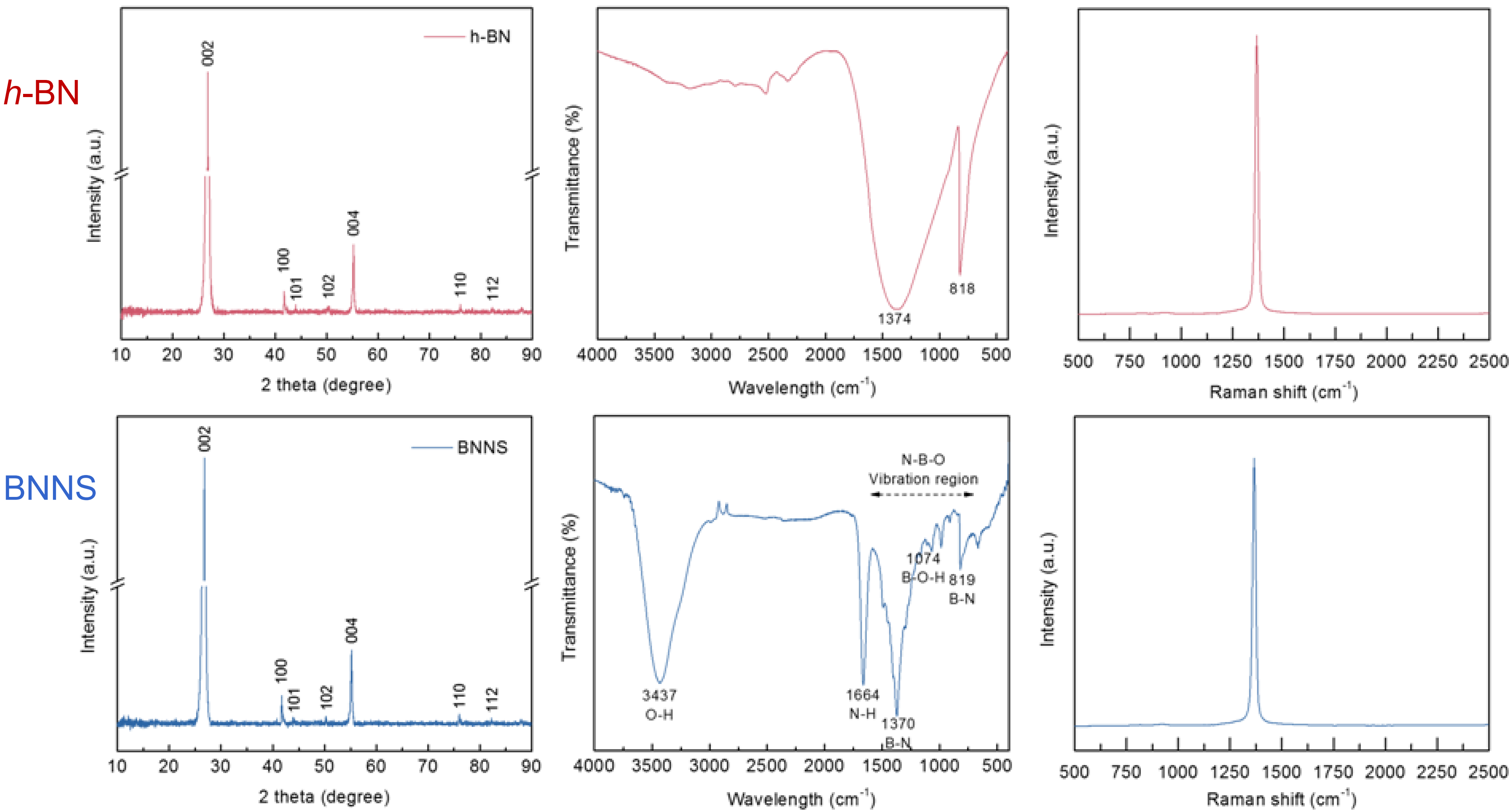




- h-BN was exfoliated by ultrasonication (1 h) and microwave irradiation (2 min).
- Surfactant SDS was used to enhance the exfoliation of *h*-BN and to improve the compatibility of BNNS with PES polymer in the following membrane preparation step.

Exfoliation of BNNS

❖ Comparisons of the XRD patterns, Raman and FTIR spectra of *h*-BN and BNNS

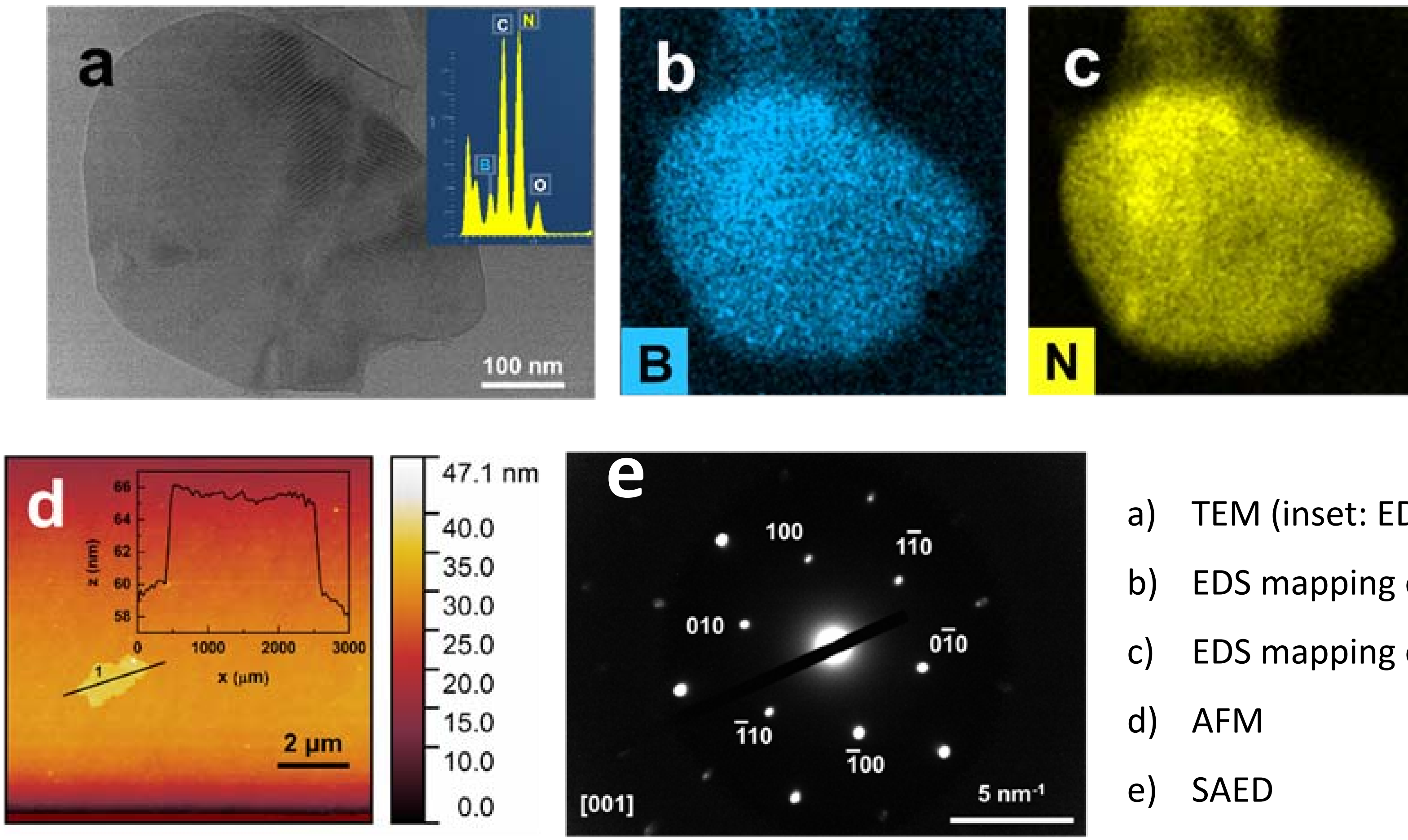


➢ XRD and Raman: successful exfoliation preserving the crystal structure and not generating impurities

➢ FTIR: generation of $B\text{-}NH_2$ and B-OH group

Exfoliation of BNNS

❖ Characterisations of the exfoliated BNNS



a) TEM (inset: EDX)

b) EDS mapping of B

c) EDS mapping of N

d) AFM

e) SAED

➢ Lateral dimension of ~ 1 μm with equal distribution of B and N atoms

➢ Thickness of 5 ~ 6 nm, equivalent to about 15 ~ 18 layers

Preparation of PBNS membranes

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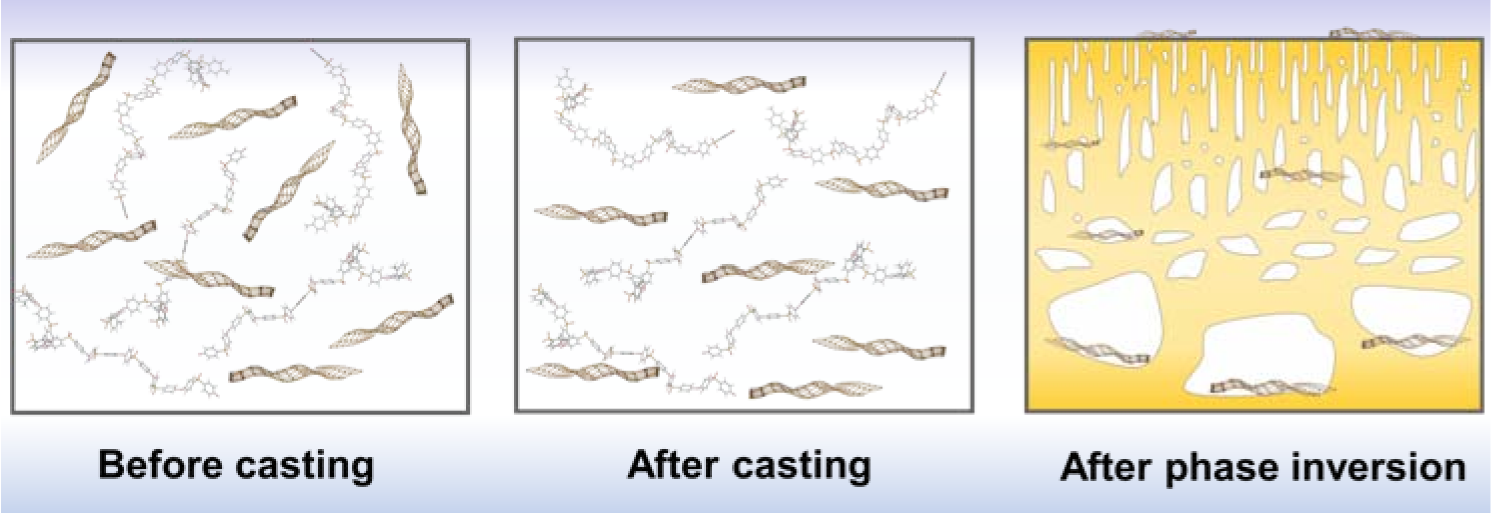
❖ Preparation of PBNS membranes by non-solvent induced phase separation

Membrane	PES (wt%)	NMP (wt%)	BNNS (wt%)
PES-pure	23.000	77.000	0.000
PBNS0.025	23.000	76.975	0.025
PBNS0.05	23.000	76.950	0.050
PBNS0.1	23.000	76.900	0.100



PBNS membrane morphology

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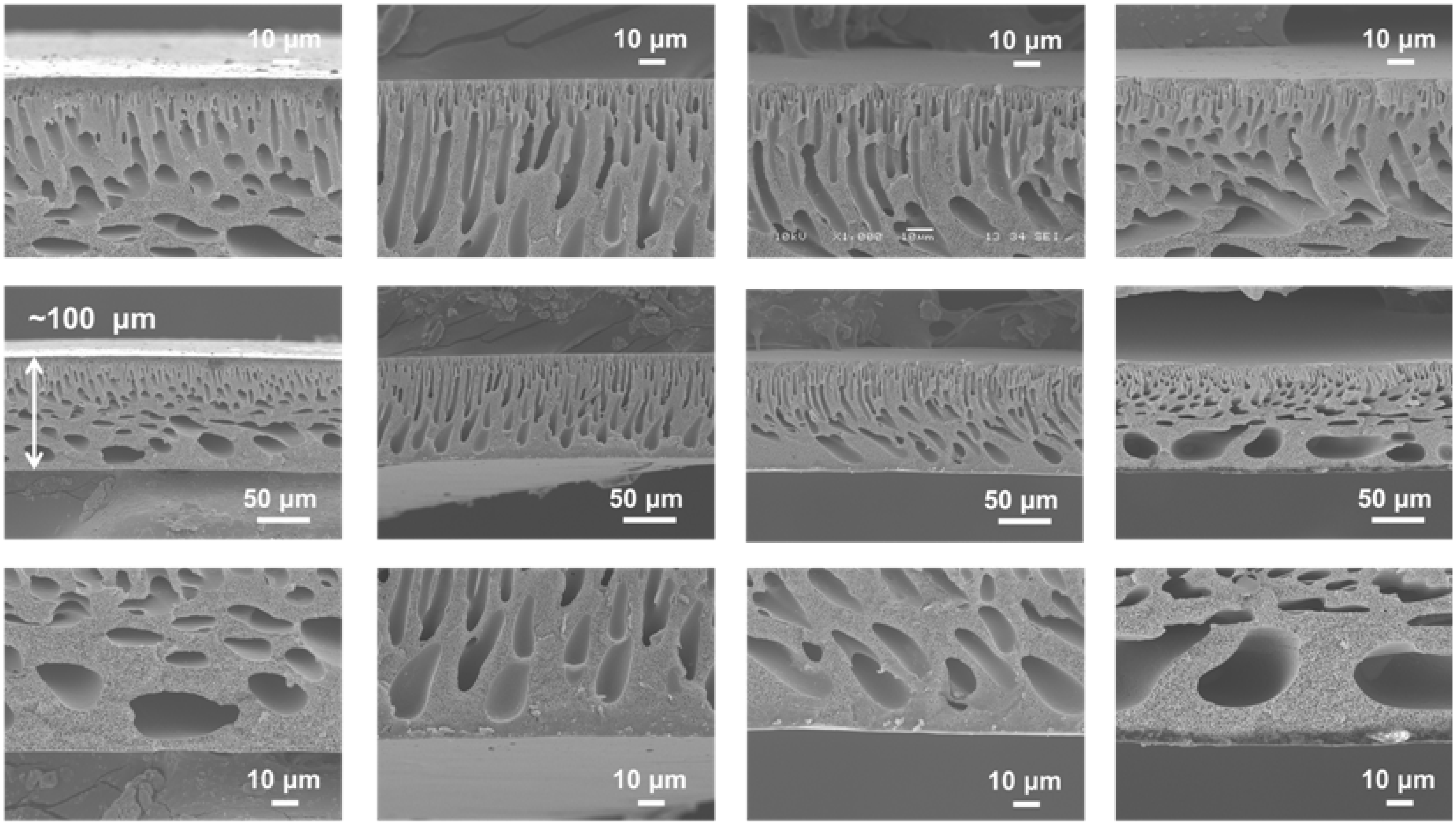
Pure PES | 0.025 wt.% | 0.05 wt.% | 0.1 wt.%



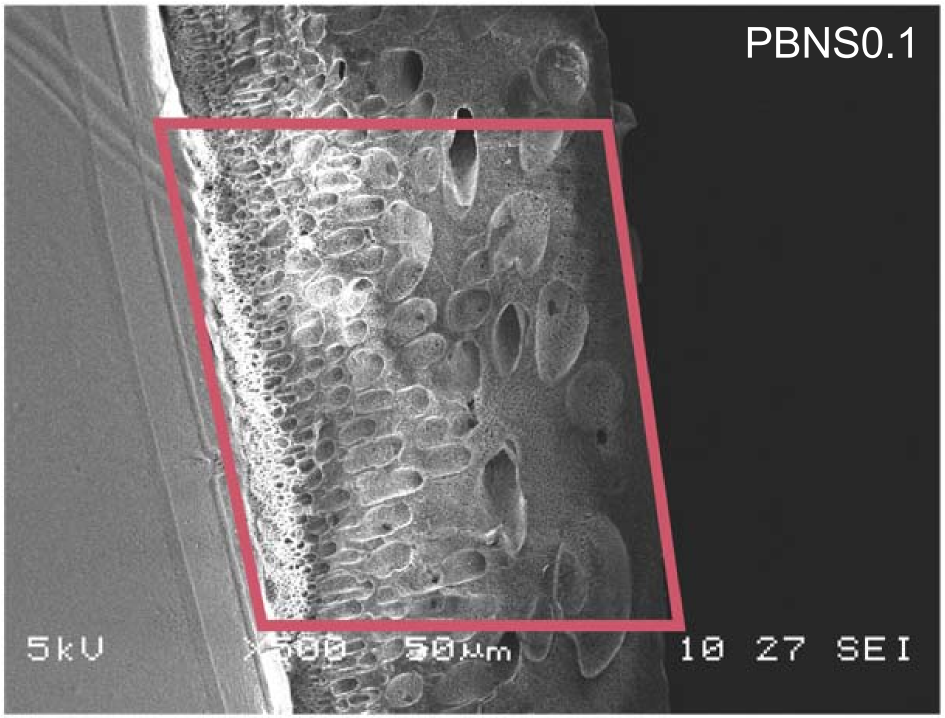
Increasing loading amount of BNNS

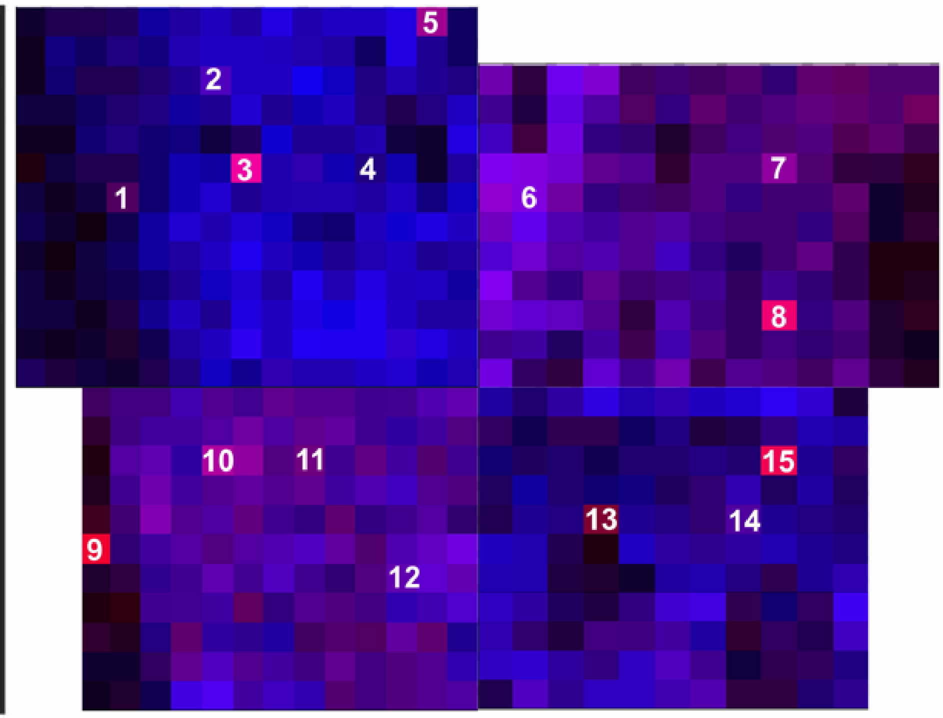
- Typical asymmetric structure with finger-like voids extending to macrovoids
- Longer "fingers" and thinner "active layer" at low loadings

Distribution of BNNS in membranes

❖ Raman mapping on the membrane cross-section

(Raman intensity at 1370 cm^{-1} is denoted as red pixels.)

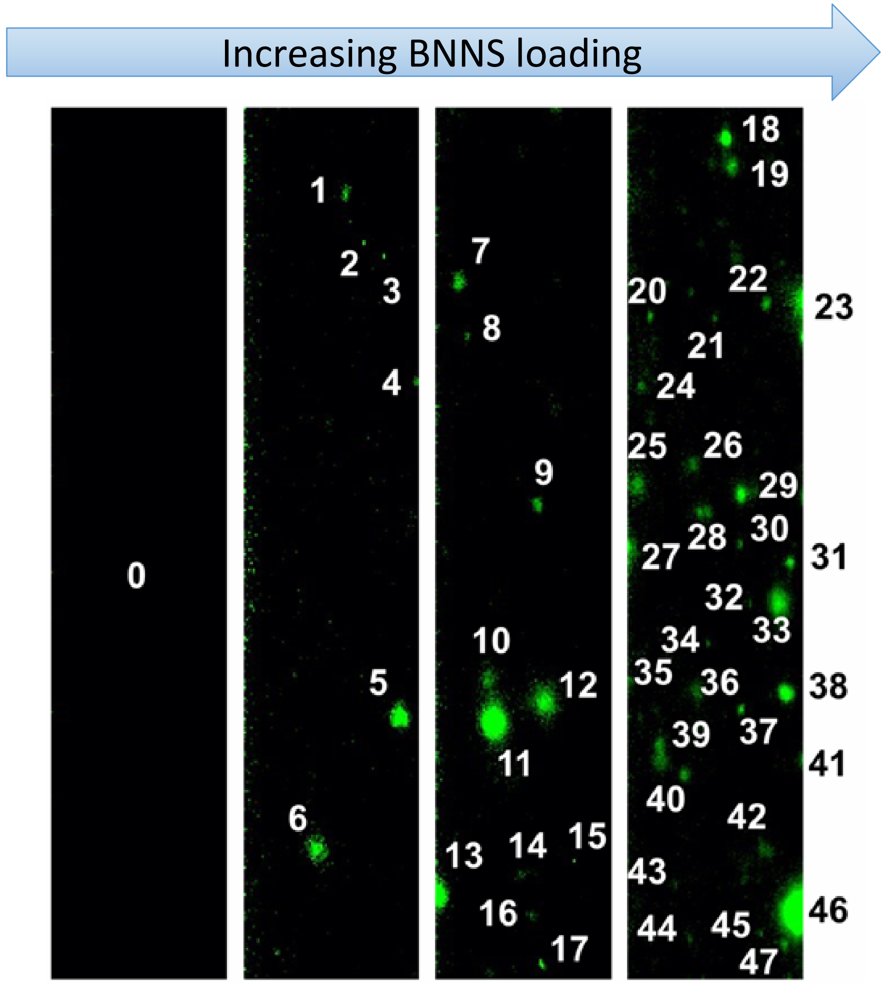




- The membrane cross-section highlighted in the red box was divided into four regions.
- BNNS is uniformly distributed throughout the membrane cross-section.
- Variations in intensity are attributed to differences in depth, size or orientation of the BNNS.

Distribution of BNNS in membranes

❖ Raman mapping on the membrane surface (500 μm × 100 μm; green spots)



➢ As the BNNS loading increases, more BNNS are detected and larger aggregates are observed on the surface.

PBNS membrane surface properties

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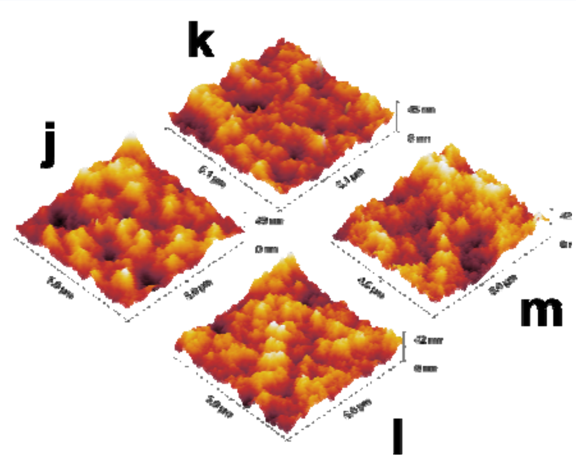
❖ Characterisations of PBNS membrane surfaces

Sample	Water contact angle (±2 °)	Diiodomethane contact angle (±2 °)	Dispersive force (mJ/m²)	Polar force (mJ/m²)	Surface free energy (mJ/m²)	Surface zeta potential (mV)	Surface average roughness, S_a (nm)	RMS height, S_q (nm)	Porosity (%)
PES-Pure	77	26	42	4.0	46 ± 1	-19.5 ± 3	6.0	7.4	52
PBNS0.025	57	31	35	16	51 ± 1	-35.7 ±3	4.9	6.2	49
PBNS0.05	56	28	36	16	52± 2	-43.8 ± 5	4.7	5.8	51
PBNS0.1	57	30	35	16	51± 2	-63.2 ± 4	5.7	7.0	50

- AFM: decreased surface roughness
- Surface zeta potential: more negatively charged
- Contact angle goniometry: increased hydrophilicity



PBNS membrane performance

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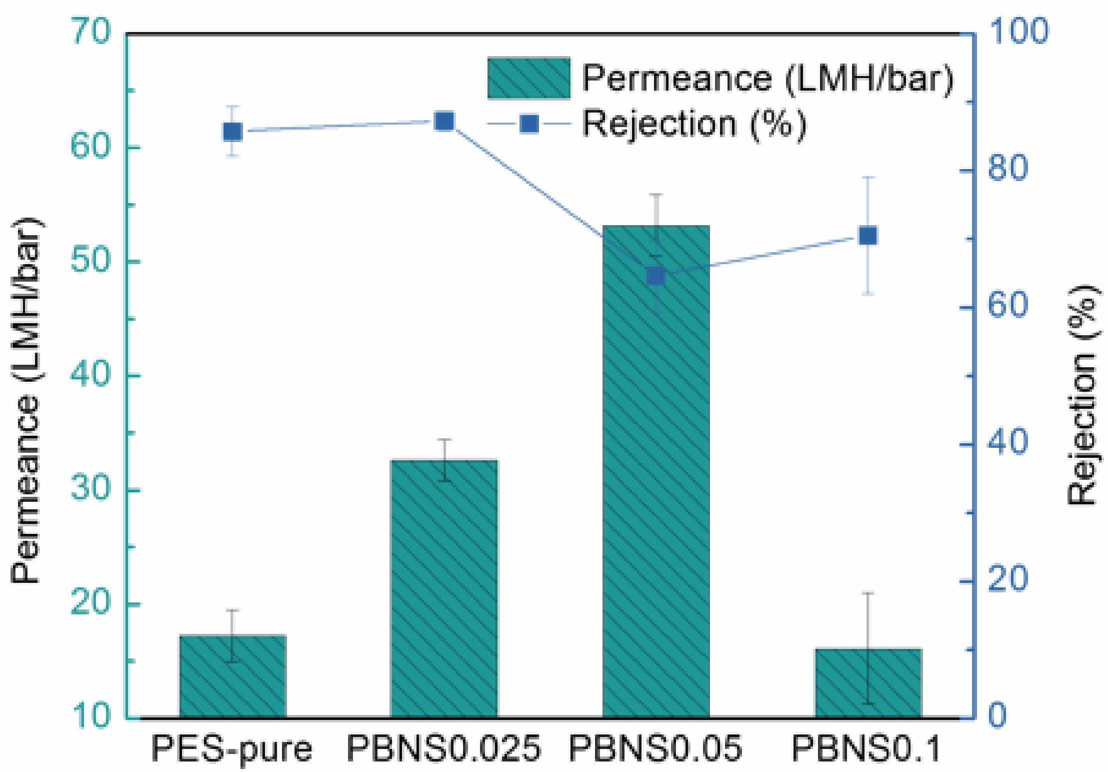
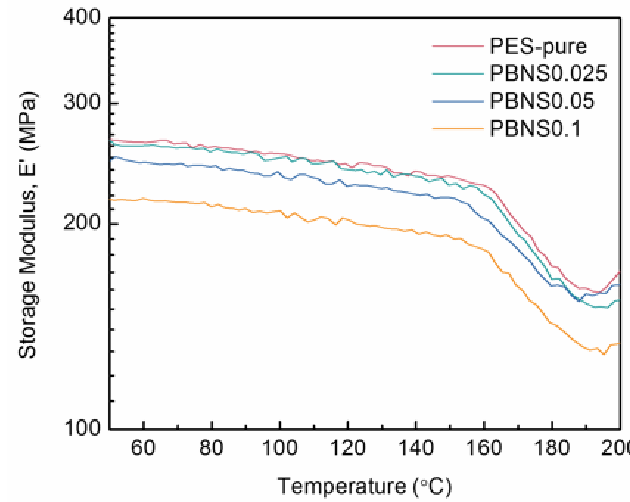
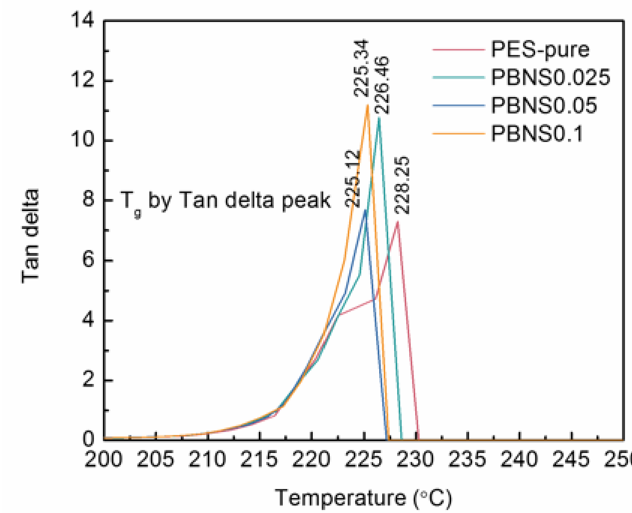
❖ Pure water permeance and rejection of Rose Bengal







- Mass balance in rejection test > 98%
- Increased permeance and decreased rejection
  - Plasticizing effect of BNNS
  - Improved hydrophilicity
  - Change in morphology

PBNS membrane performance

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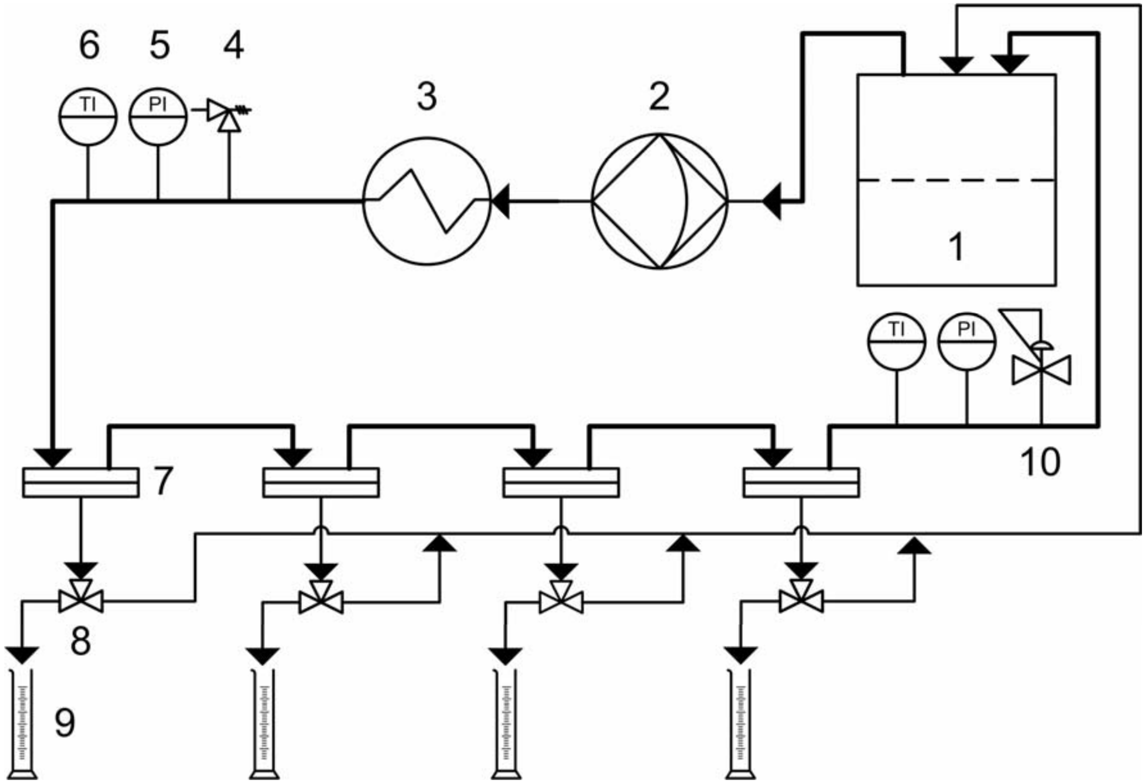
❖ Fouling test with humic acid



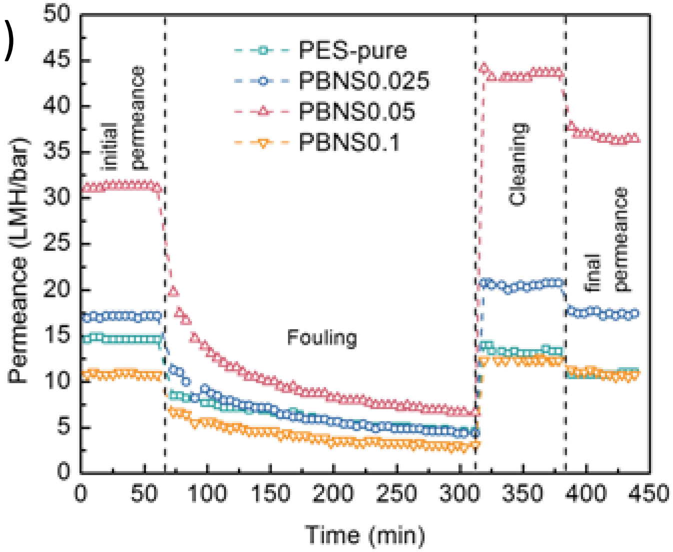
1) Solvent tank
2) Pump
3) Oil bath
4) Pressure relief valve
5) Pressure gauge
6) Thermocouple
7) Flat sheet membrane cell
8) Three-way valve
9) Measuring cylinder
10) Back pressure regulator

- Compact the membranes at 10 bars
- Measure the initial pure water permeance at 8 bars
- Foul the membranes with humic acid at 4 bars for 4 hours
- Perform cleaning-in-place for 1 hour
- Measure the pure water permeance after cleaning
- Perform second fouling and cleaning cycle on the same membrane samples

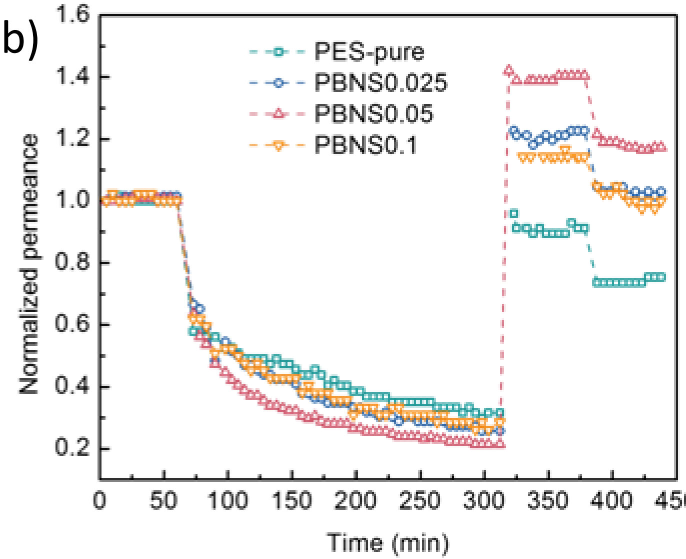
PBNS membrane performance

❖ Fouling test with humic acid – first cycle

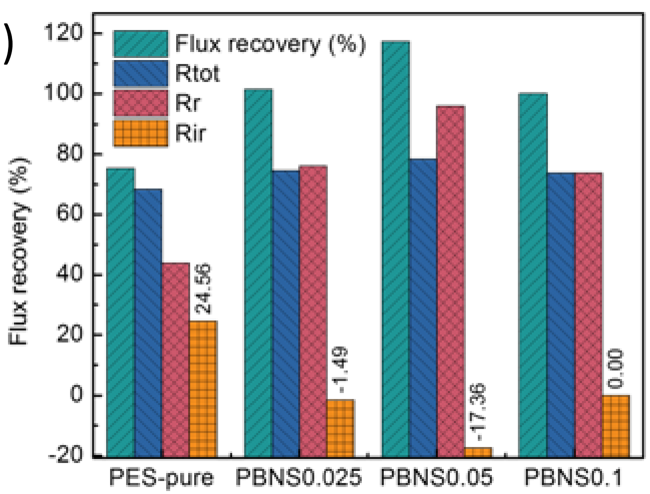
a)



b)



c)



a) Fouling behaviour in the first fouling and cleaning cycle

b) Normalized water permeance in the first fouling experiment

c) Flux recovery, total fouling ratio, reversible fouling ratio and irreversible fouling ratio

➢ PBNS membranes have extremely small irreversible fouling and show nearly full flux recovery due to increased hydrophilicity, lower surface roughness and higher surface charges

PBNS membrane performance

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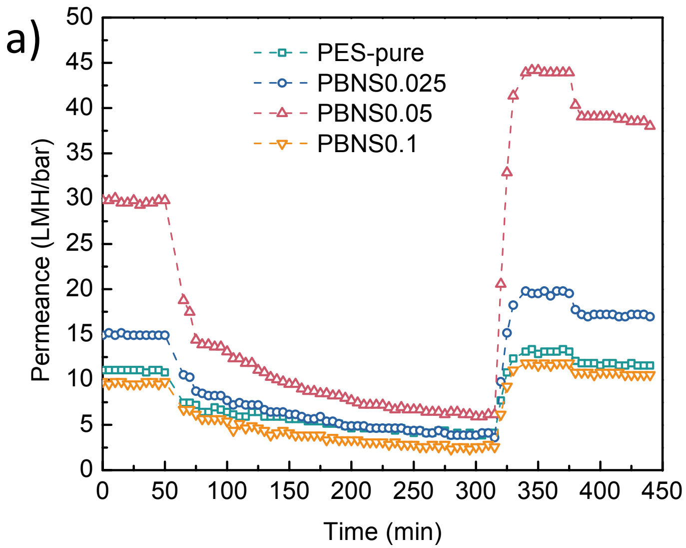
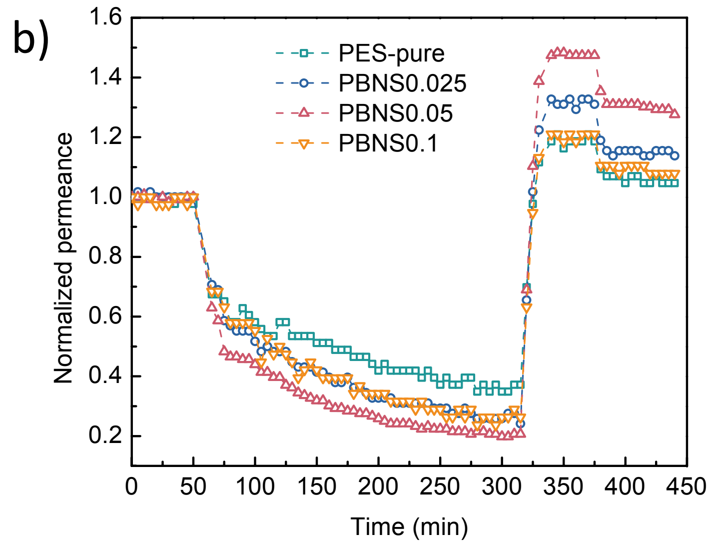
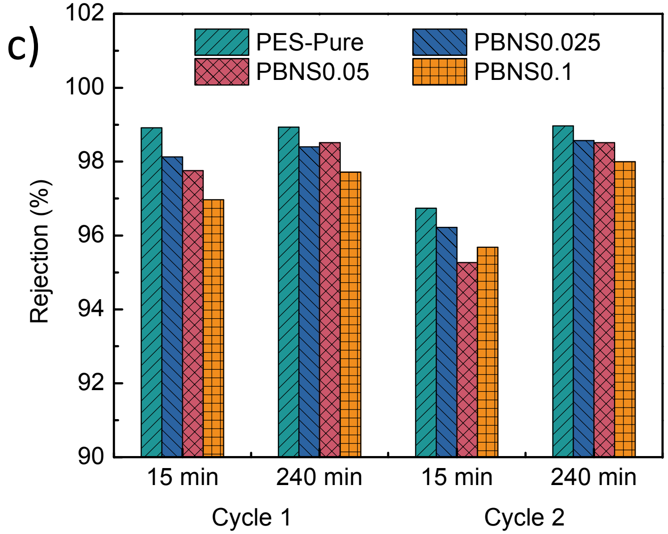
❖ Fouling test with humic acid – second cycle







a) Fouling behaviour in the second fouling and cleaning cycle

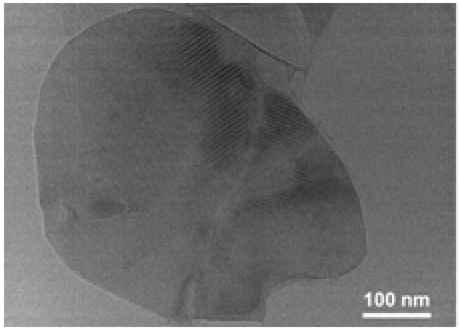
b) Normalized water permeance in the second fouling experiment

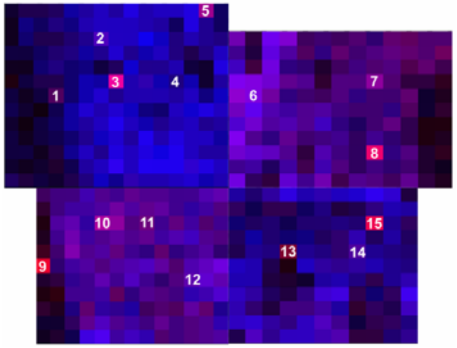
c) Humic acid rejection in the two fouling cycles

- ➢ Excellent fouling resistance and water recovery maintained after two fouling cycles
- ➢ Consistent rejection of humic acid (first cycle > 97%, second cycle > 95%)

Conclusions

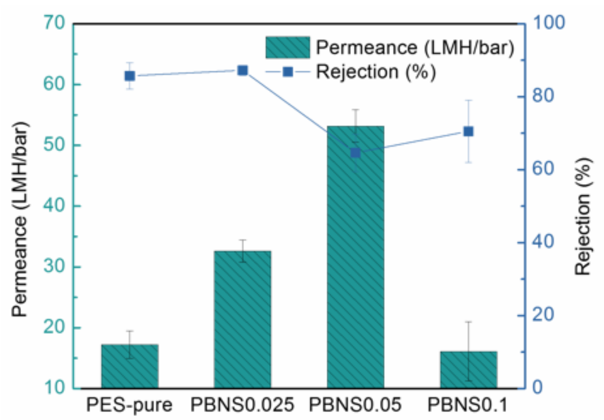
BNNS with lateral size of ~ 1 µm and thickness of 5 ~ 6 nm were obtained by a gentle *h*-BN exfoliation method based on ultrasonication and microwave irradiation.

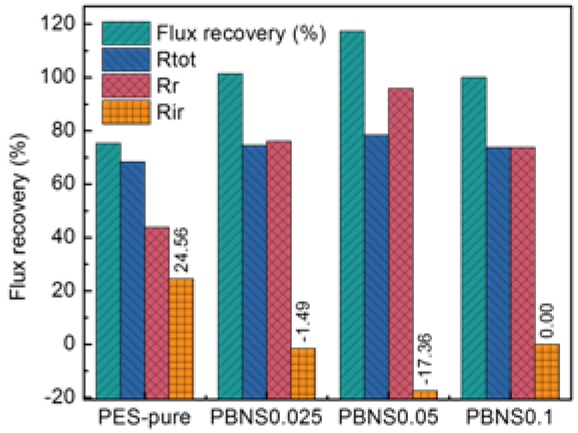




Uniform distribution of BNNS in the PBNS membranes was achieved, as confirmed by Raman mapping.

Compared to pure PES membranes, the PBNS membranes showed increased water permeance while maintaining comparable dye rejection.





PBNS membranes displayed excellent fouling resistance and water recovery in the two fouling and cleaning cycles.

Z. Low et al., *J. Membr. Sci.*, **2018**

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Acknowledgement

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The authors wish to dedicate this paper to their colleague, Dr Darrell Patterson.

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