



HUAZHONG UNIVERSITY of SCIENCE and TECHNOLOGY

School of Chemistry and Chemical Engineering

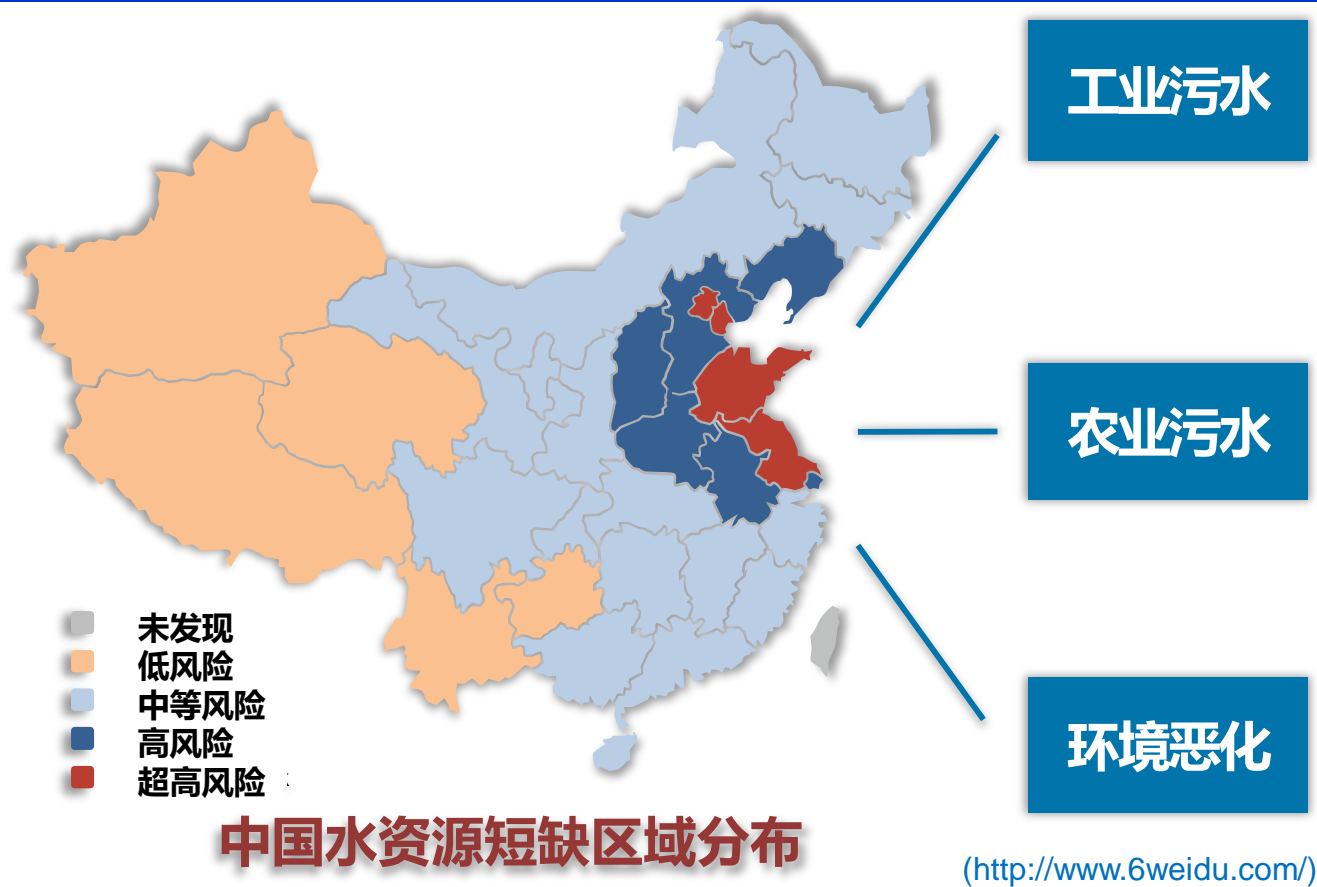
1037 Luoyu Road, Wuhan, China, 430074

超薄复合纳滤膜的制备及其 在有机溶剂纯化和水处理中的 应用

王 艳

华中科技大学 化学与化工学院

研究背景



理想分离膜材料的要求

➤ 化学相容性：保持膜的稳定性

耐酸碱：防止分离过程中，以及清洗过程中的水解

耐高温：高通量带来的温度升高和清洗的需要

➤ 机械稳定性

耐压：膜孔径小，要保持高通量就必须施加较高的压力；

➤ 生物相容性：防止生物大分子的变性

➤ 高通量

$$J_w = \frac{V}{A \cdot t \cdot \Delta P} \quad J = \frac{m}{A \cdot t}$$

➤ 高截留率

$$R_s = (1 - \frac{C_p}{C_F}) \times 100\% \quad \alpha = \frac{y_{w,1} / y_{w,2}}{x_{w,1} / x_{w,2}}$$

➤ 成本低

分离膜的类型

- **按孔径大小/应用:**

微滤膜、超滤膜、反渗透膜、纳滤膜、正向渗透、渗透汽化、气体分离、电渗析等

- **按材料分:**

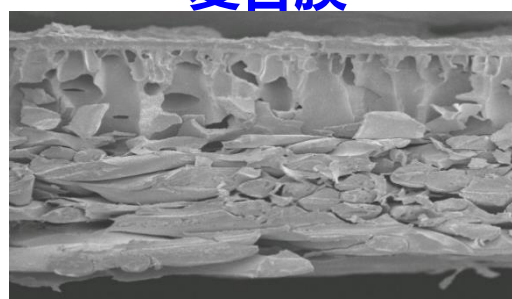
有机（聚合物）膜、无机材料膜

- **按膜结构:**

对称性膜、不对称膜、复合膜



复合膜



致密选择层
不对称多孔层
支撑层

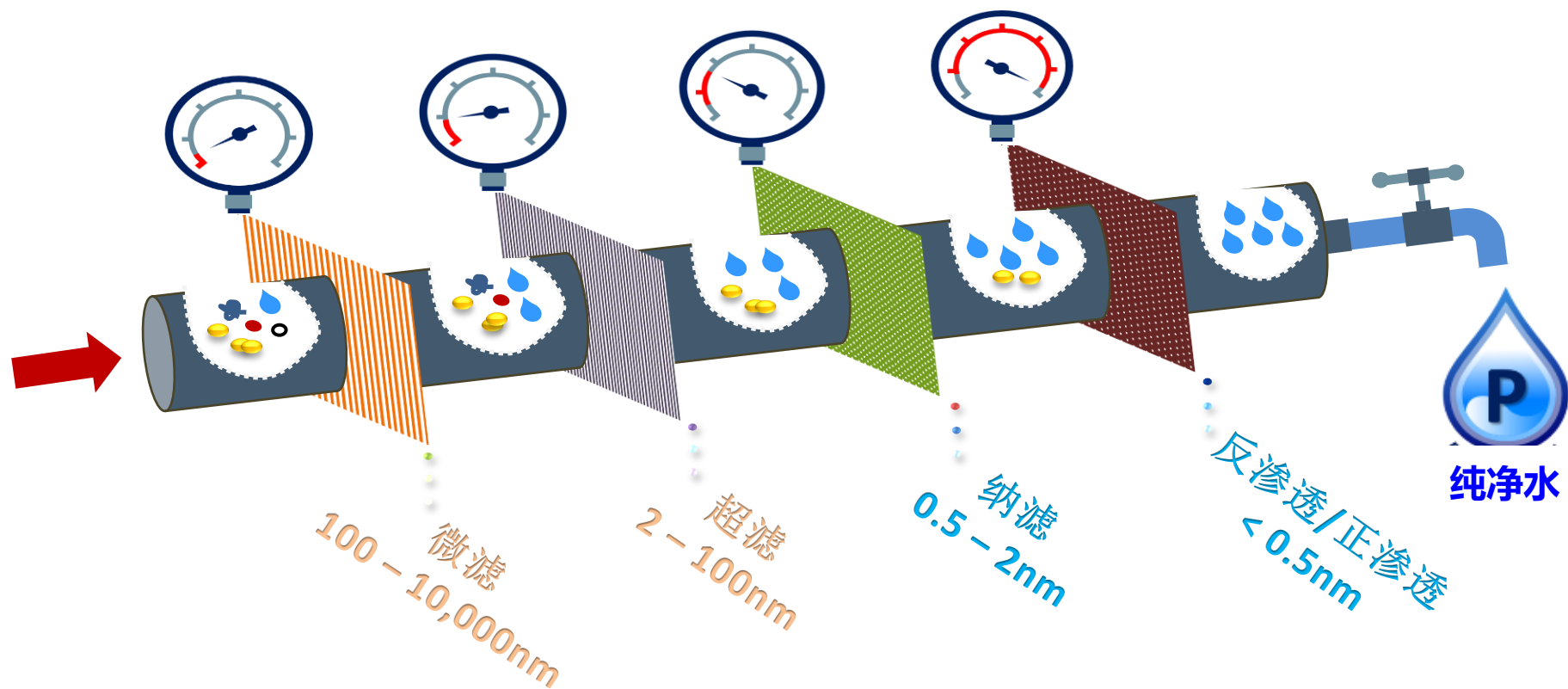
分离效能主要或完全由很薄的皮层决定，传质阻力小，其透过速率较对称膜高得多。

研究背景

固体颗粒 ○
大分子 𠂇

有机化合物 红点
多价离子 黄点

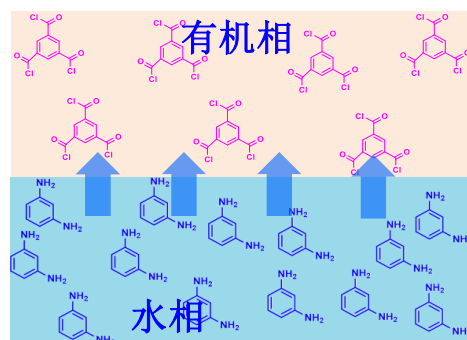
单价离子 黄点
水 水滴



研究背景

界面聚合法制备聚酰胺超薄复合膜 (TFC 膜)

- ✓ 容易制备
- ✓ 较高溶质截留率
- ✓ 较高水通量
- ✓ 较宽的操作温度和pH范围



界面聚合
(IP)

选择层

薄、致密、亲水、
低污染倾向

支撑层:

疏松、亲水、较低的
孔曲率、机械稳定性

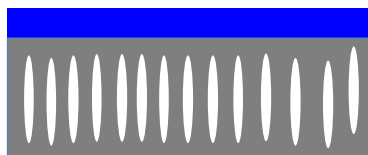
- ✗ 亲水性不够
- ✗ 两层亲和性问题
- ✗ 相对疏水的PA选择层
- ✗ 粗糙的峰谷表面形貌
- ✗ 支撑层严重的内浓差极化

选择层和支
撑层可分别
优化与改性!

理想的TFC 膜

- ✓ 优异的溶剂渗透通量和溶质截留率
- ✓ 较强的耐酸、碱、溶剂的性能，能保持长期稳定性
- ✓ 在较广的有机溶剂范围内保持良好稳定性

基膜性能优化

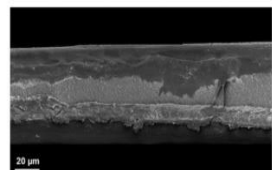


支撑层

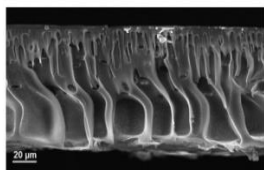
疏松、亲水、低孔曲率、机械稳定度、化学稳定性

聚合物本体功能化改性

Sulphonated Polyethersulfone (SPES)
(12 wt %)
Sponge morphology-hydrophilic

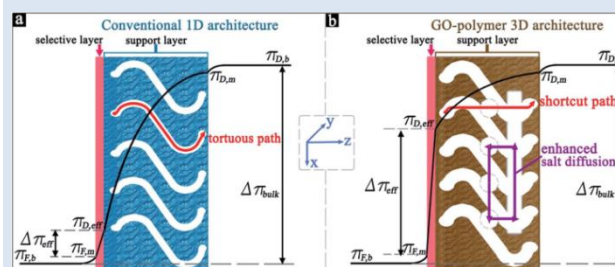


Polyethersulfone (PES) - (12 wt %)
Macrovoids structure

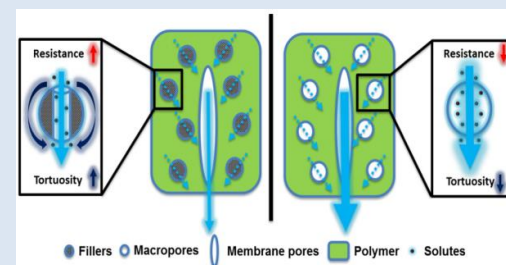


Desalination 389 (2016) 129–136

亲水添加剂共混/掺杂

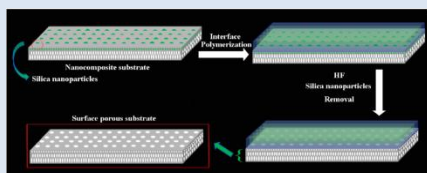


J. Mater. Chem. A, 5 (2017) 12183–12192

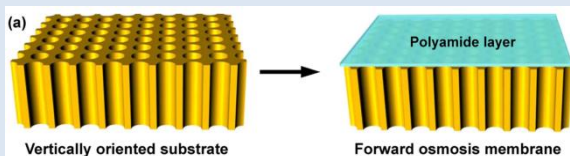


J. Membr. Sci., 492 (2015) 392–399

支撑层制备工艺设计

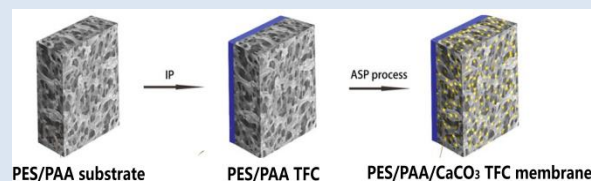


J. Membr. Sci., 529 (2017) 47–54

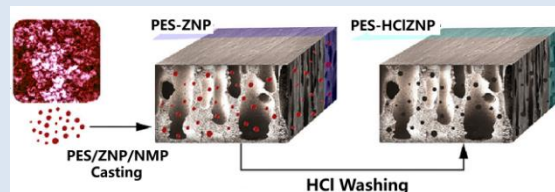


Ind. Eng. Chem. Res., 55 (2016) 5327–5334

基膜后处理矿化/刻蚀

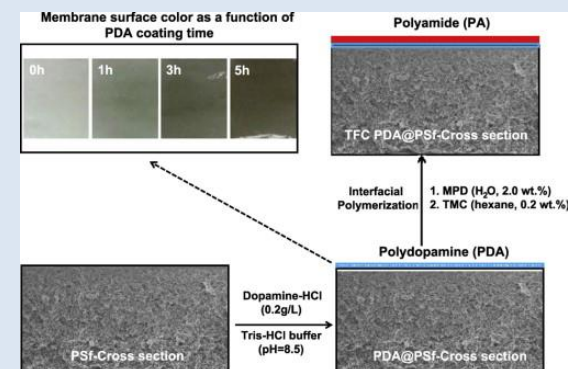


Environ. Sci. Technol., 2018, 52, 2704–2716



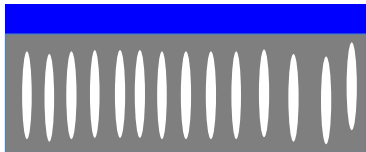
Sci. Rep., 2016, 6: 19593–19602.

表面亲水化处理



Chem. Eng. Sci., 80 (2012) 219–231

基膜性能优化



支撑层

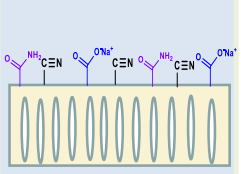
疏松、亲水、低孔曲率、机械稳定度、化学稳定性

提升亲水性、降低ICP

引入亲水通道、提高通量

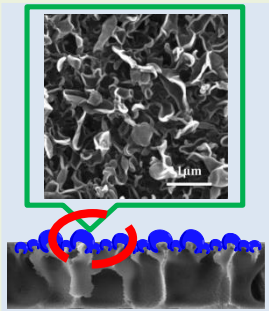
提升耐溶剂性能

表面碱处理

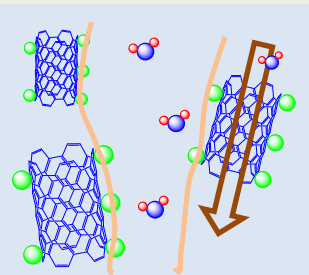


PAN基膜表面亲水改性

全氟磺酸共混

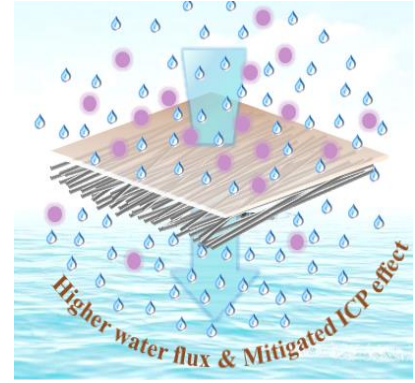


SiO₂@MWNTs掺杂

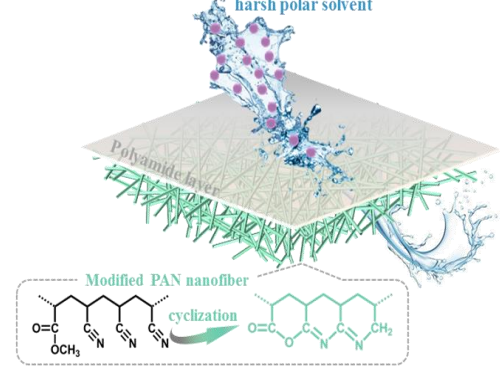


利用碳管无阻力传质通道
抑制ICP

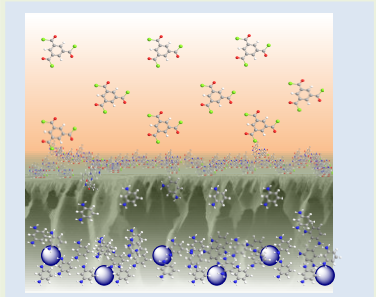
有序排列的纳米纤维基膜



热致环化改性



p-TiO₂改性



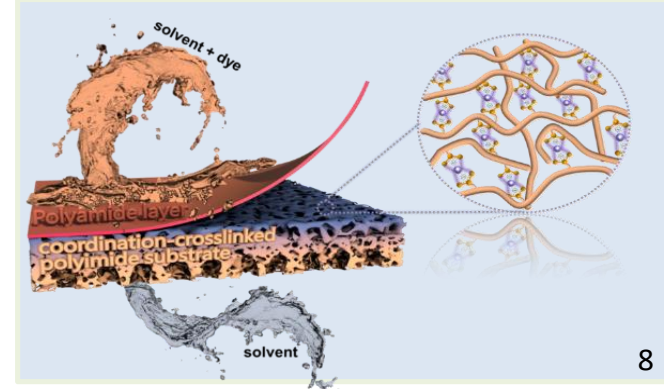
限制IP过程胺单体扩散
PA层更加平滑致密

温敏凝胶PNIPAM引入



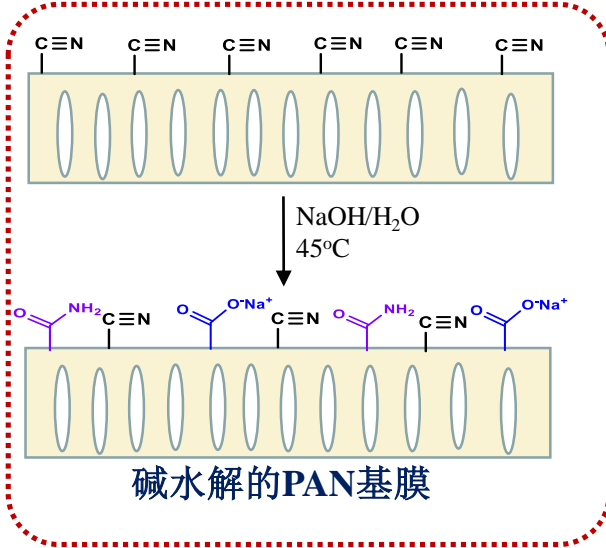
提升基膜孔道通透性
提升膜通量

碱水解+金属离子络合交联

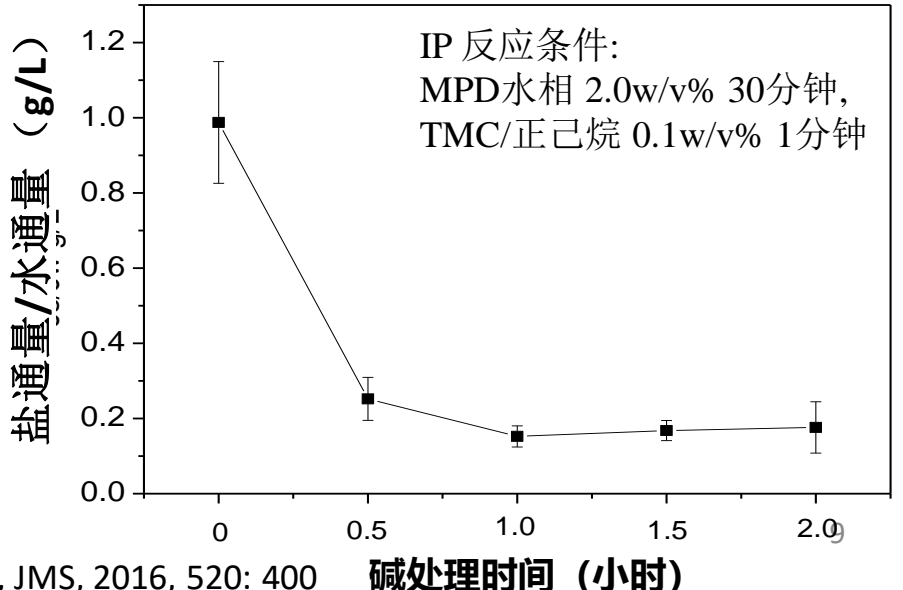
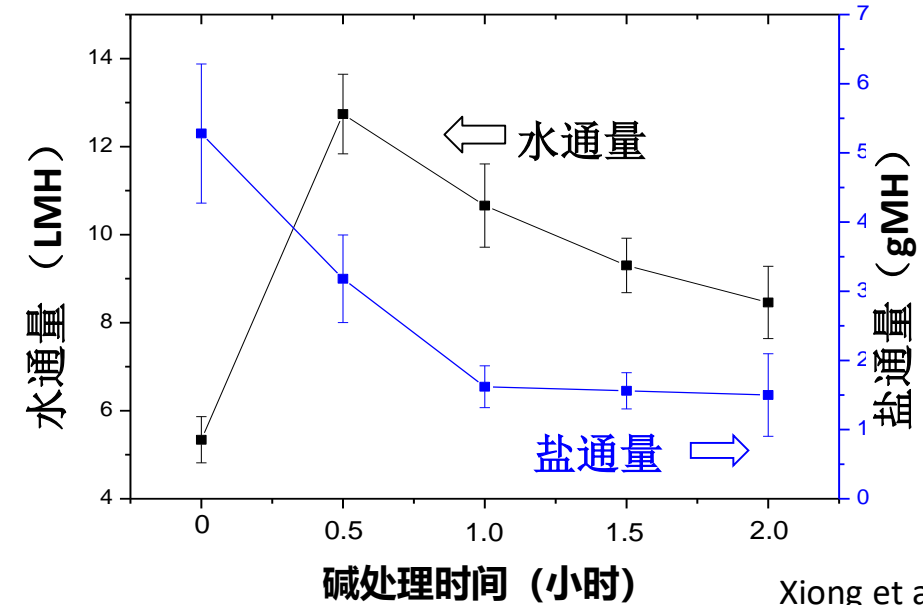


基膜性能优化

PAN 基膜的表面亲水性改性

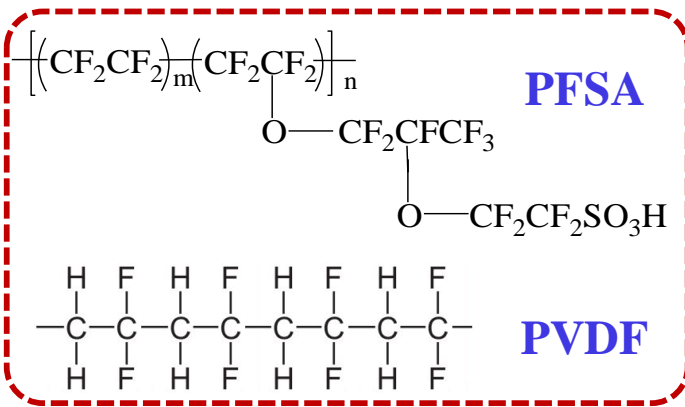


改性基膜	水解时间	水接触角 (°C)	平均孔径 (nm)	MWCO (kDa)	纯水通量 (LMH/bar)
HPAN0	0	71	16.7	465	136.6
HPAN0.5	0.5h	38	13.1	378	113.4
HPAN1.0	1.0h	35	12.7	352	54.3
HPAN1.5	1.5h	32	12.2	349	47.4
HPAN2.0	2.0h	34	11.9	333	45.1

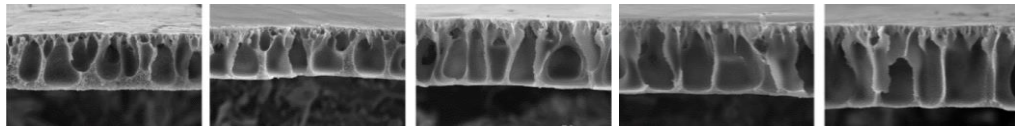


基膜性能优化

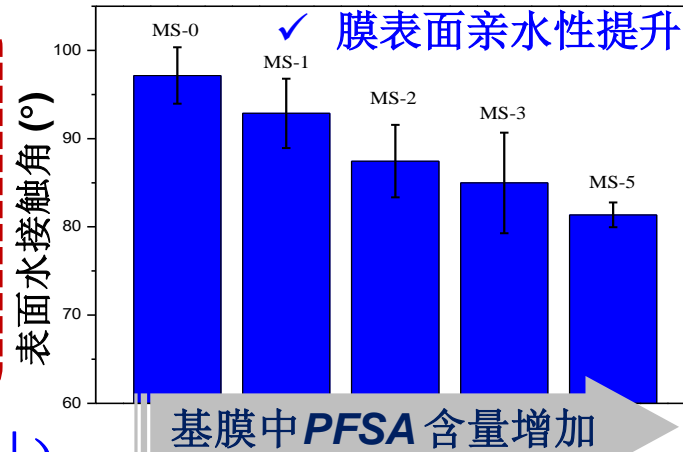
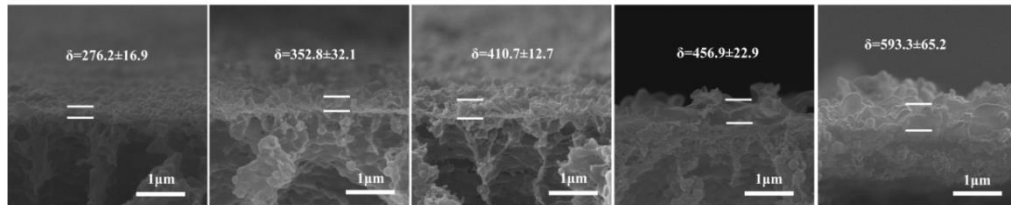
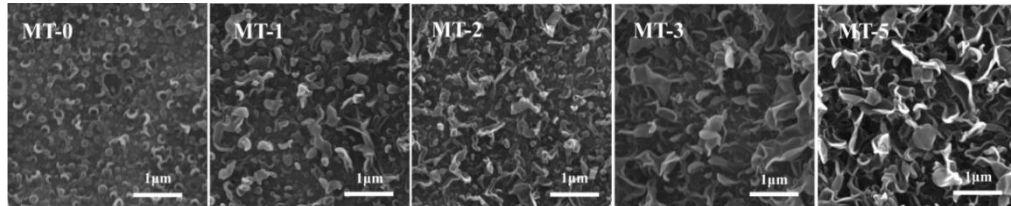
PVDF/PFSA共混基膜



✓ 较低的孔曲率 (结构参数 $S\downarrow$)



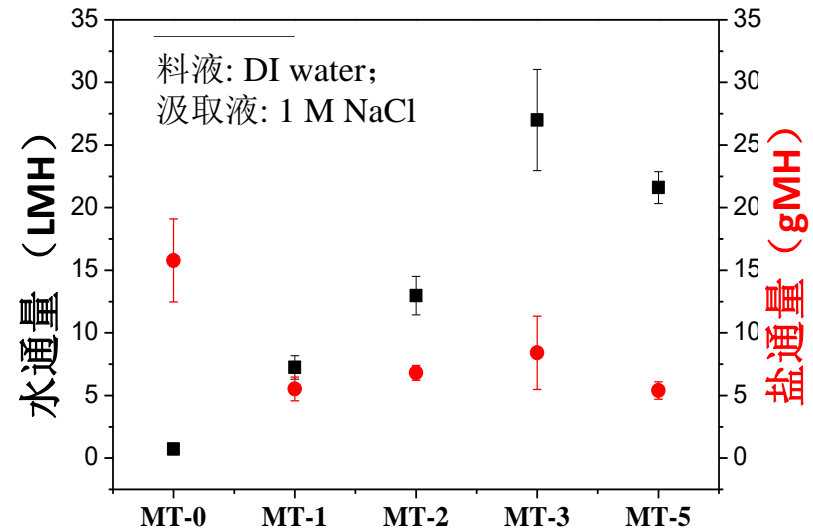
✓ 更显著的 ridge-and-valley 表面形貌结构



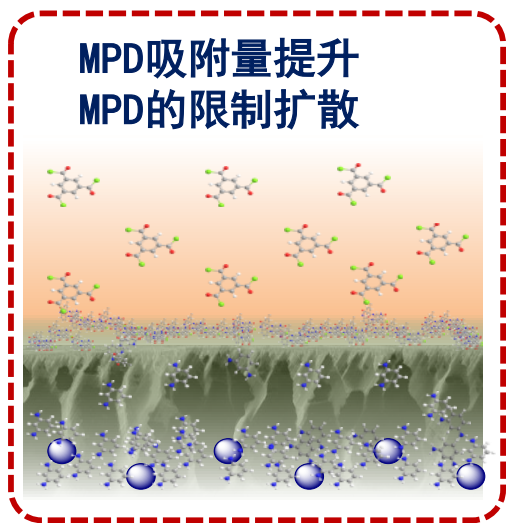
✓ 基膜孔隙率增大

MS-0	72.4 ± 0.3 %
MS-1	81.8 ± 0.4 %
MS-2	85.8 ± 0.5 %
MS-3	86.7 ± 0.6 %
MS-5	88.4 ± 0.1 %

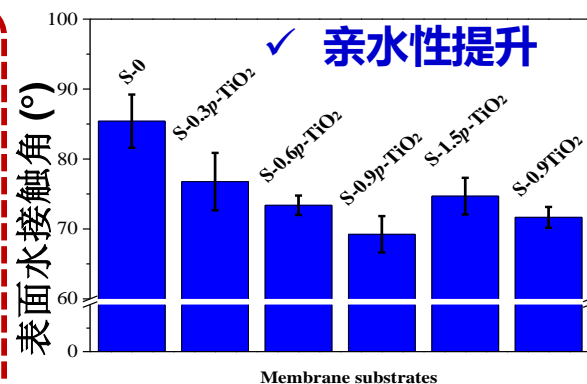
✓ 正渗透分离性能提升 (FO mode)



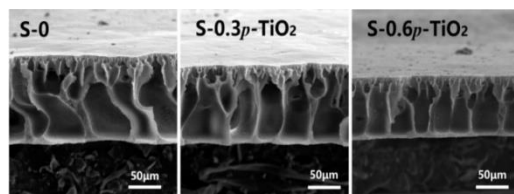
p-TiO₂掺杂改性PVDF 基膜



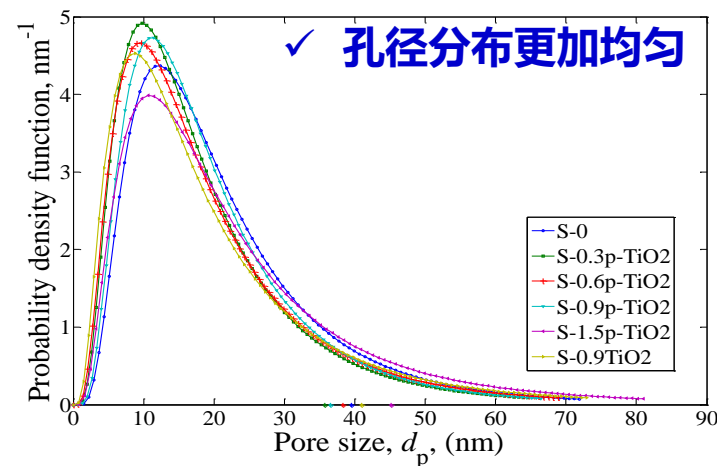
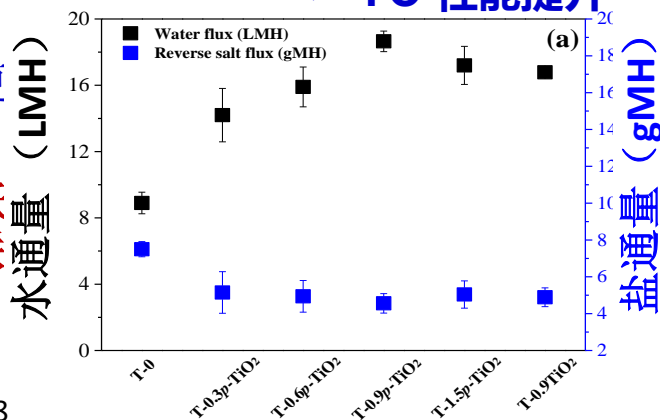
- 提升了基膜亲水性: 促进MPD单体更多更均匀的吸附
- 限制了IP过程中MPD向有机相扩散: 形成更平滑致密的PA层
- 膜具更高水通量与更低通量衰减率: PA层交联度更大、表面更平滑



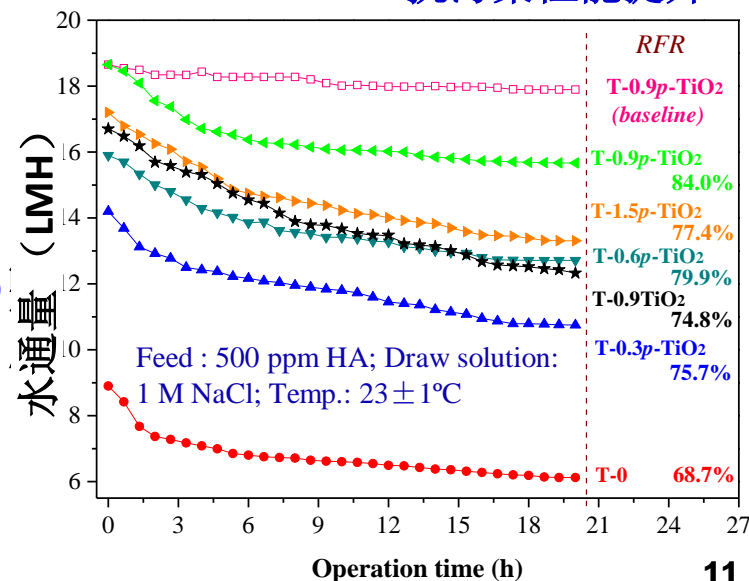
孔道结构更规整



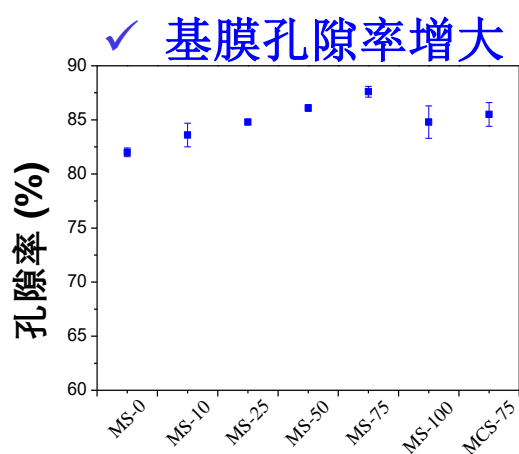
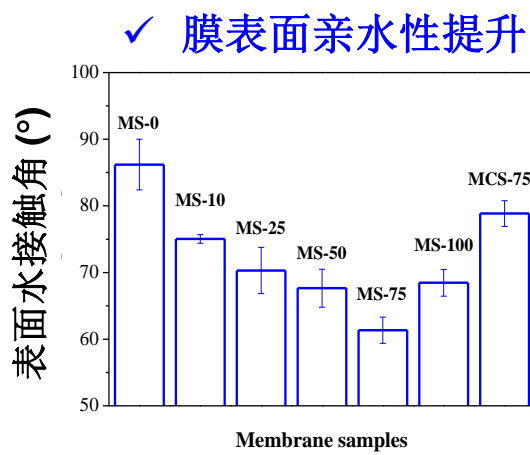
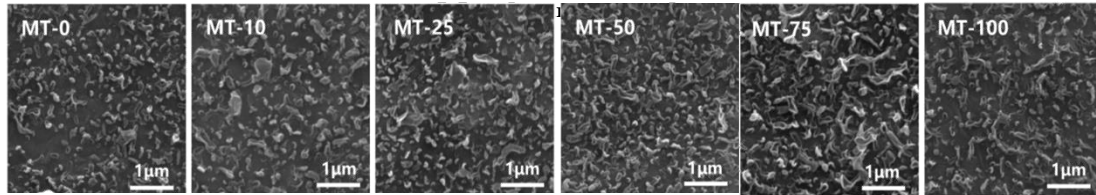
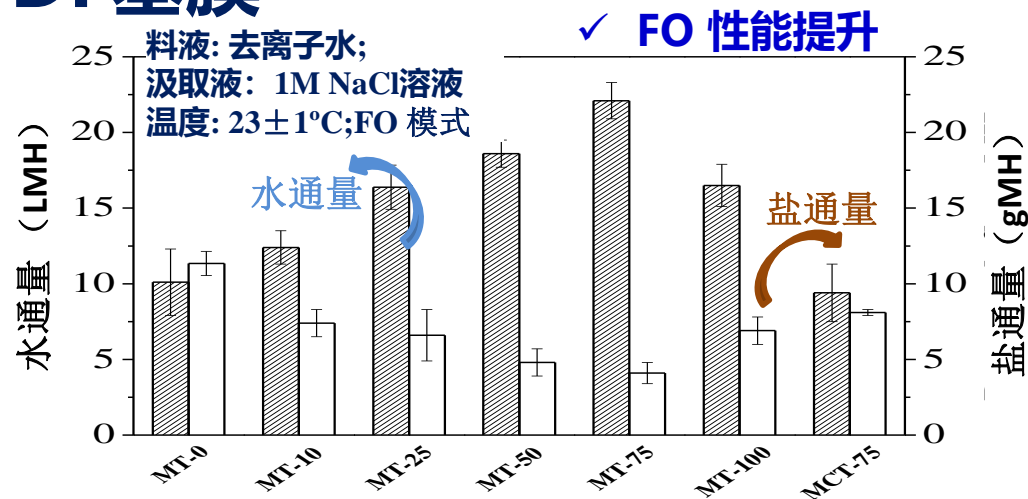
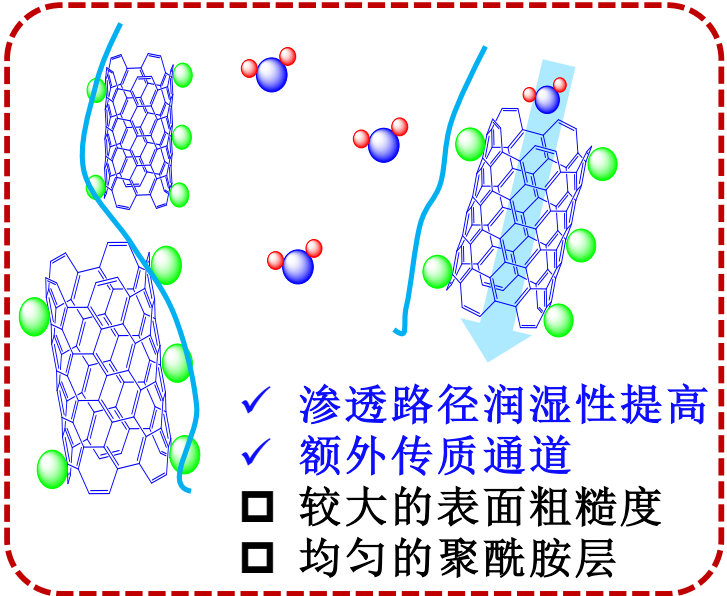
FO 性能提升



抗污染性能提升



SiO₂@MWNT改性PVDF基膜



✓ **孔径减小**

μ (nm)	σ
21.4	1.38
20.2	1.46
17.0	1.51
16.0	1.52
13.1	1.61
18.7	1.69
22.4	1.53

Xuan Zhang et al.
JMS 2018, 564,
328

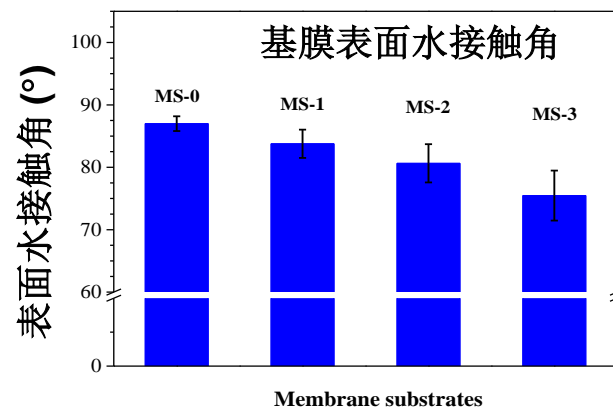
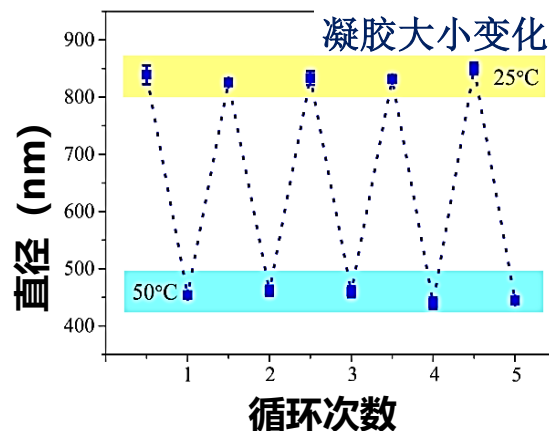
基膜性能优化

温度响应型微米凝胶掺杂改性PVDF基膜

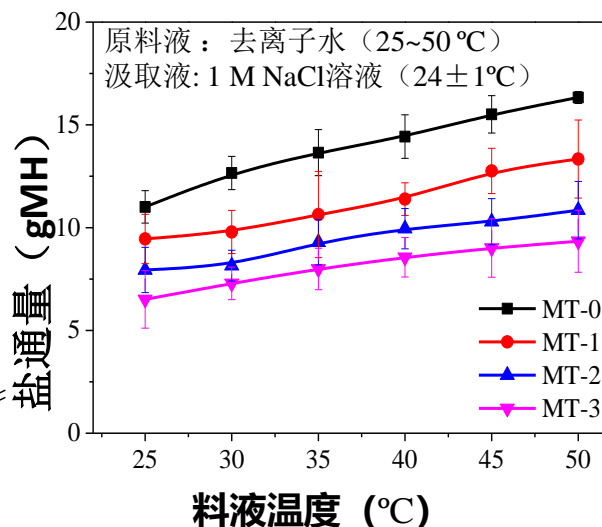
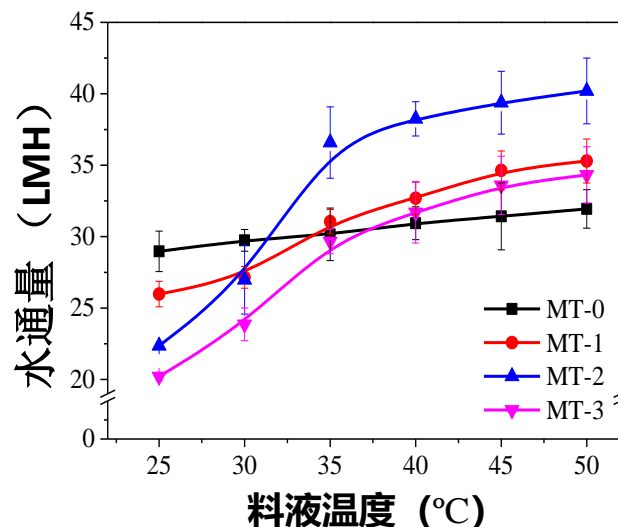


铸膜液: PVDF/PFSA/PNIPAM
(16/3/x, wt.%)

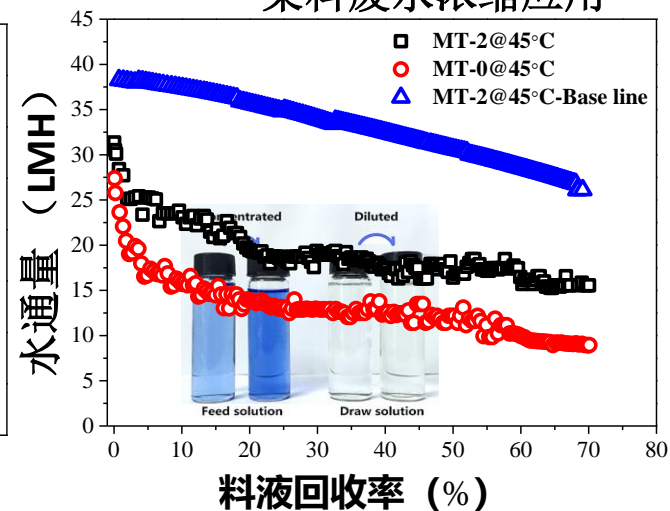
MS-x: “x” 表示铸膜液中微米凝胶
质量百分比



TFC膜FO性能



染料废水浓缩应用

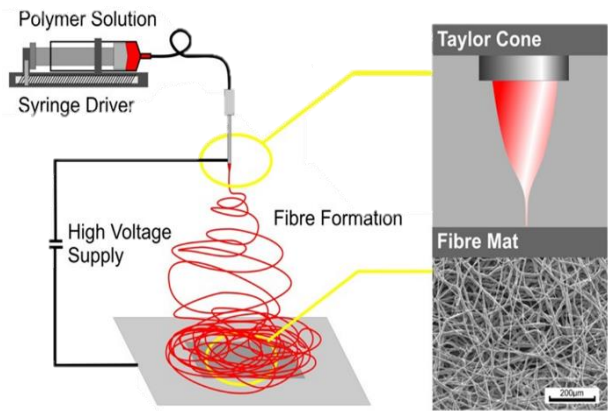


- 料液: 50 ppm RB-19, 500 ppm NaCl, 500 ppm Na_2SO_4 ; 45 °C (印染工业排出废水~50 °C)
- 汲取液: 1 M NaCl溶液, 室温 (24 ± 1 °C)

基膜性能优化

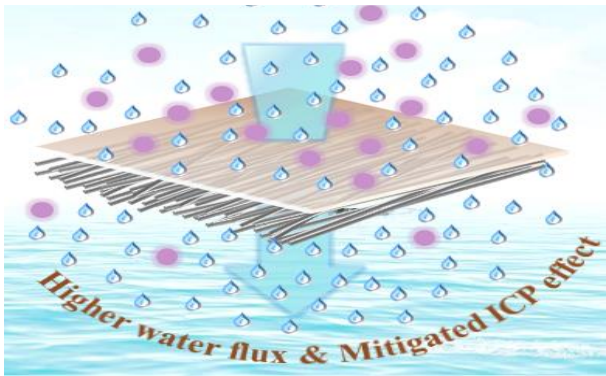
具狭缝孔的取向纳米纤维基膜

纳米纤维膜



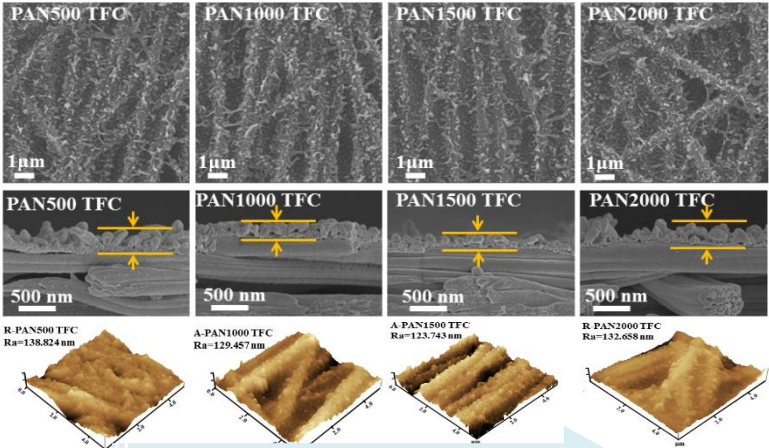
- ✓ 比表面积大
- ✓ 孔隙率高
- ✓ 贯穿的孔结构
- ✓ 曲率低
- ✗ 机械强度不佳
- ✗ 膜表面孔径偏大

取向纳米纤维基的TFC膜



- ✓ 提高基膜机械性能
- ✓ 优化膜孔结构
- ✓ 操作简单

不同拉伸速度取向纳米纤维基膜的TFC膜形貌



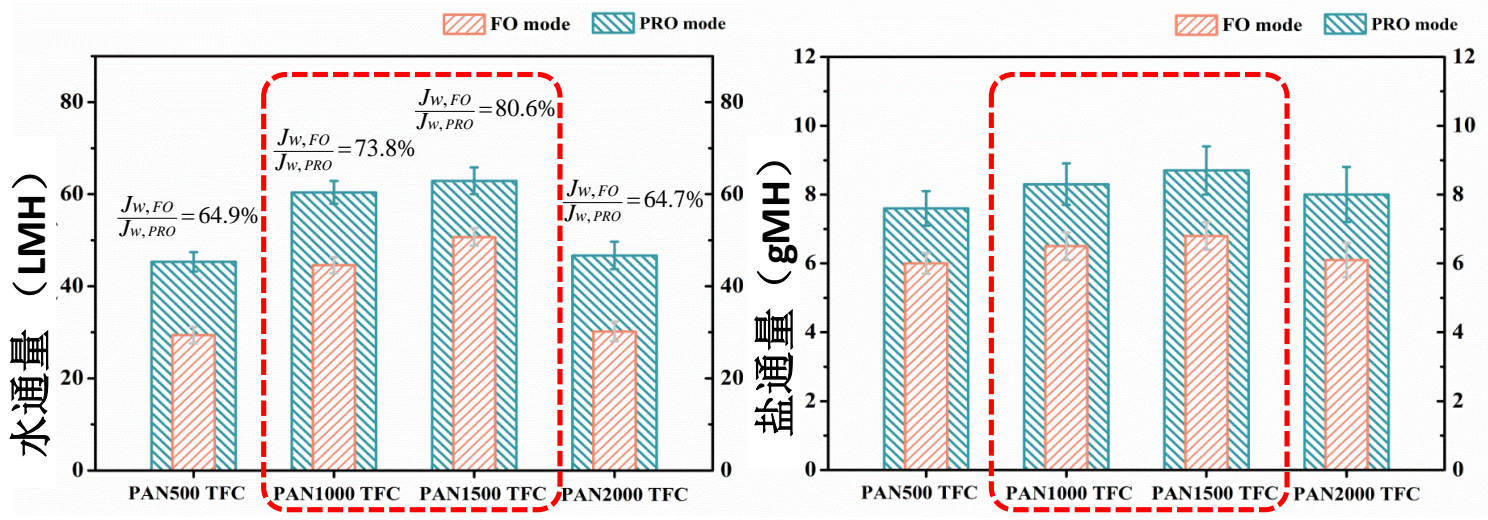
拉伸速度提高

纳米纤维基膜	拉伸速度 (rpm)	纳米纤维取向度 (%)	孔隙率 (%)	平均孔径 (µm)
PAN500	500	28.3	81.2 ± 0.6	0.61 ± 0.03
PAN1000	1000	89.6	83.6 ± 0.9	0.96 ± 0.05
PAN1500	1500	92.1	84.3 ± 0.8	1.11 ± 0.09
PAN2000	2000	30.4	81.7 ± 0.9	0.83 ± 0.06

基膜性能优化

具狭缝孔的有序纳米纤维基膜

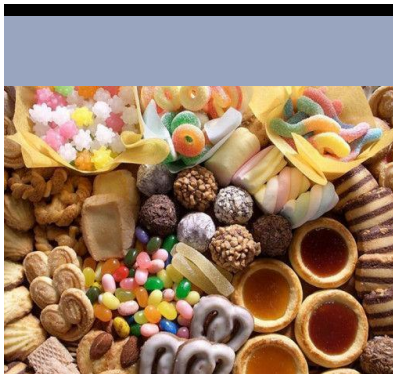
TFC膜FO分离性能



- ✓ 水通量提升
- ✓ 内浓差极化效应减弱

纳米纤维基膜	J_w (LMH) (FO/PRO)	J_s/J_w (g/L) (FO)	S (μm)	文献
有序 PAN 纳米纤维(PAN1500)	50.7/62.9	0.13	86.4	本工作
PAN	29.3/51.1	0.24	168	J. Membr. Sci. 2017, 523, 205.
PVDF	28.0/47.6	0.46	325	Sep. Purif. Technol. 2013, 118, 727
PEI/MWCNTs (MWCNTs 掺杂)	32.8/61.3	0.07	310	J. Membr. Sci. 2016, 499, 352.
PEI/SiO ₂ NPs (SiO ₂ NPs 掺杂)	42/72	0.13	174	Desalination, 2017, 401, 152.
聚酰亚胺	13.6/20.3	0.35	350	Appl. Surf. Sci. 2018, 427, 1.
nylon 6,6 改性 PVDF	22.0/31.0	0.17	193	J. Membr. Sci. 2016, 499, 352.
Nylon 6,6	21.0/27.0	0.24	-	J. Membr. Sci. 2014, 457, 162.15

有机溶剂纳滤膜的基膜优化



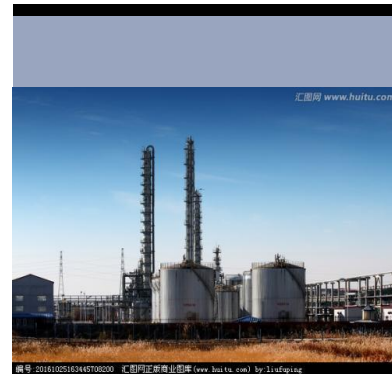
食品工业



精细化学品



药物生产

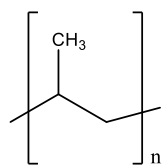


石化企业

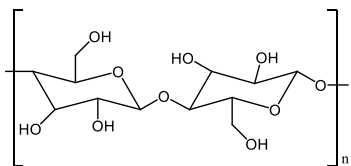
工业生产诸多过程均需要使用大量有机溶剂，直接排放会污染环境，导致水体富营养化等环境问题，因此需要**回收利用**

优异的耐有机溶剂的基膜材料

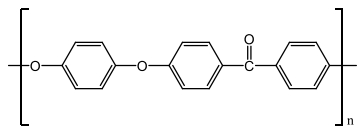
固有高耐溶剂性聚合物



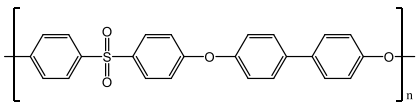
聚丙烯 (PP)



纤维素



聚醚醚酮 (PEEK)



聚苯酚 (PPSU)

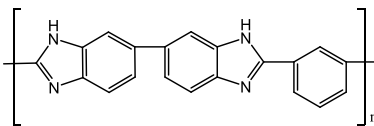
紫外诱导交联、气相交联

后处理改性

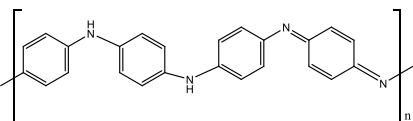
热交联

溶液浸泡化学交联

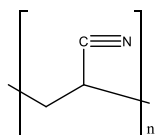
常规聚合物



聚苯并咪唑 (PBI)

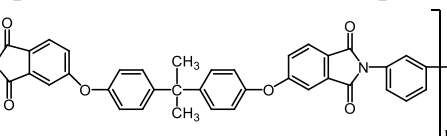
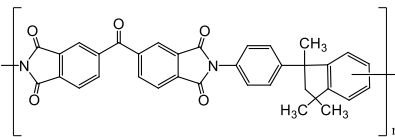
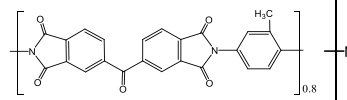
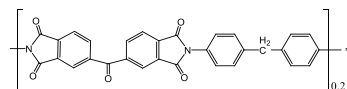


聚苯胺 (PANi)



聚丙烯腈 (PAN)

聚酰亚胺类 (PI)



交联剂

卤代烃类 (DCX、DBX、DBB)、
戊二醛、环氧树脂类 (DEO)、
硫酸以及均苯三甲酰氯

戊二醛、氯代烃类 (DCX)

水合肼

二胺类 (HDA、EDA、
PDA、BDA、MPD、
ODA、XDA)、三胺类
(DETA)、多胺类
(HPEI)

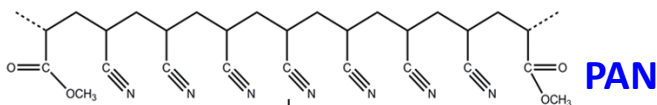
挑战

- 易产生有机废液且耗时长
- 交联后的基膜整体渗透通量降低

基膜性能优化

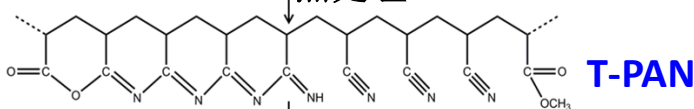
环化改性聚丙烯腈纳米纤维基膜用于有机溶剂纳滤

线性PAN链

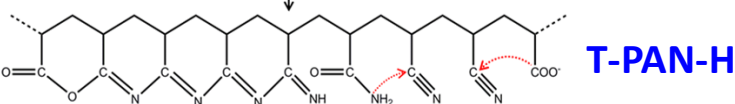


热处理

杂环PAN链



碱处理



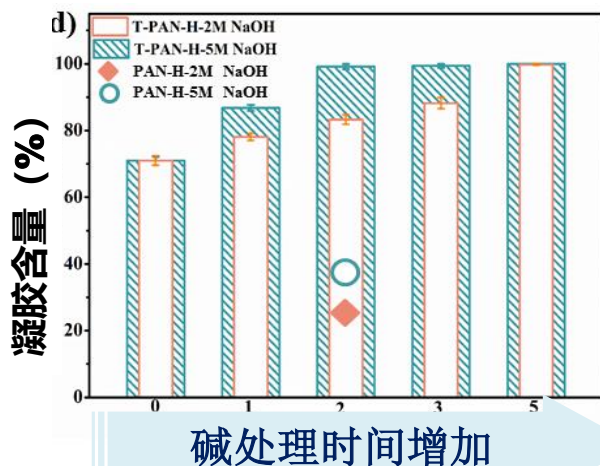
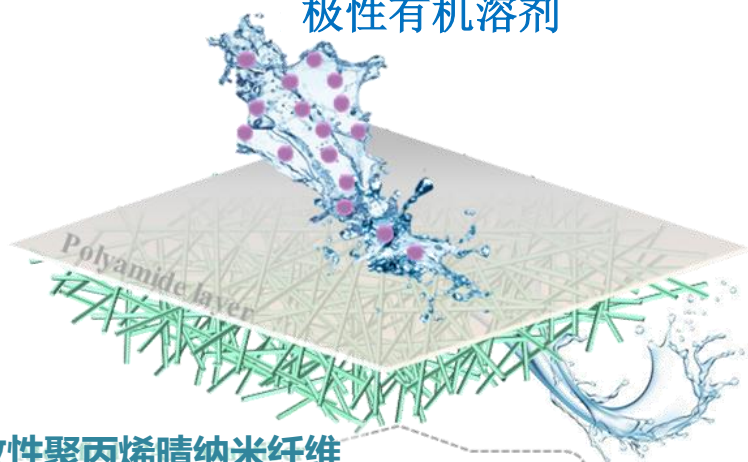
① 线性PAN链通过热处理部分转化为环状结构

② 碱性水解诱导进一步环化

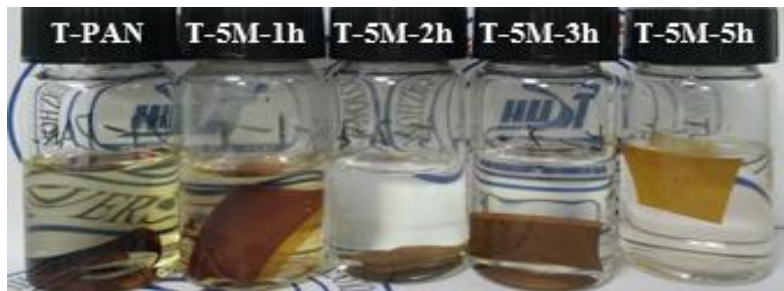
改性聚丙烯腈纳米纤维



极性有机溶剂

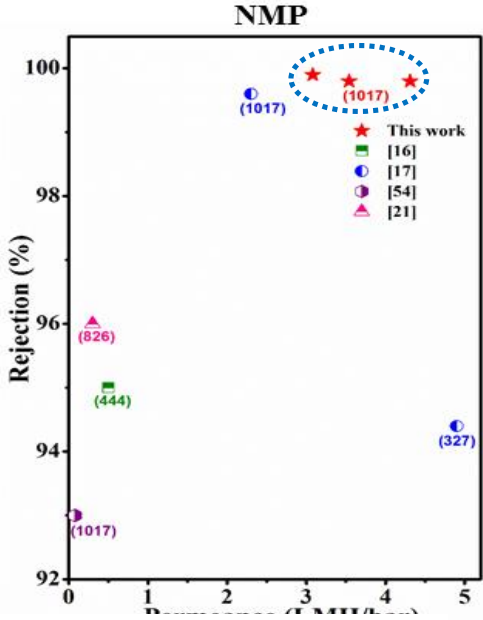
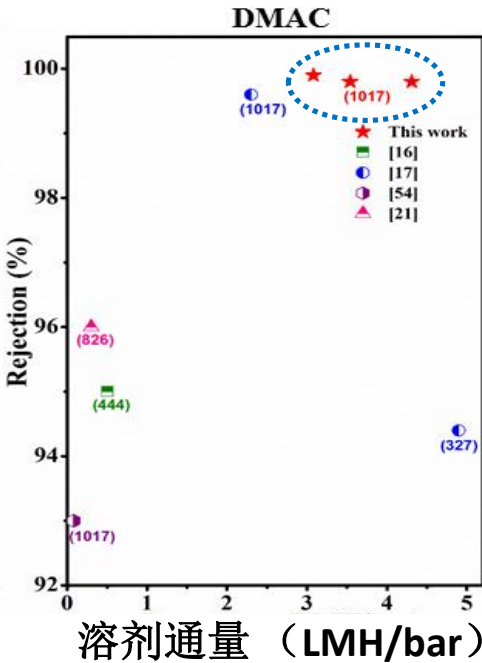
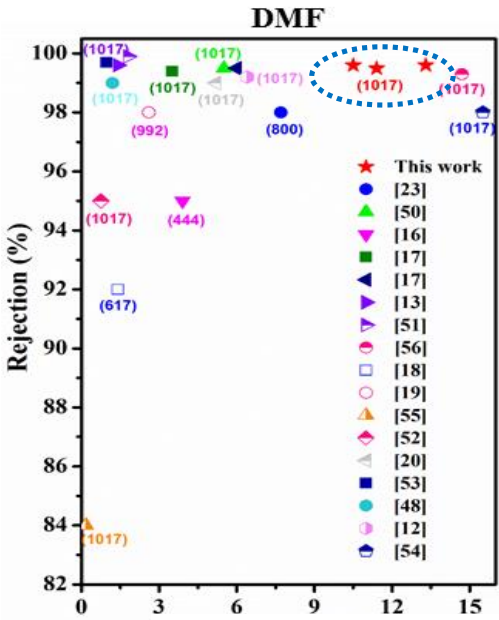


DMF溶剂中浸泡28小时的基膜

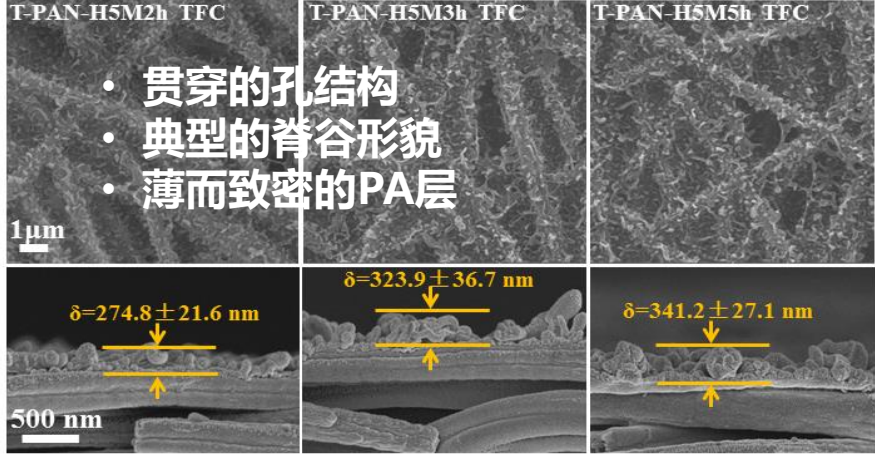
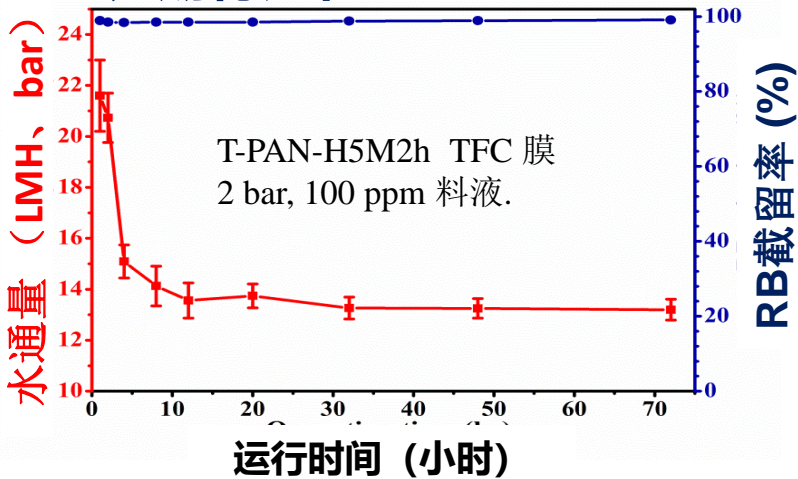


环化改性PAN纳米纤维基膜用于有机溶剂纳滤

有机溶剂
纳滤性能
对比



长期稳定性

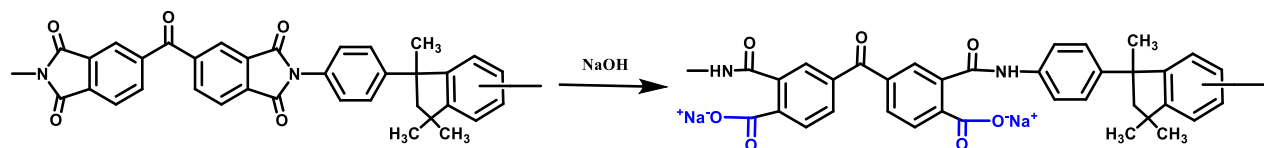


基膜性能优化

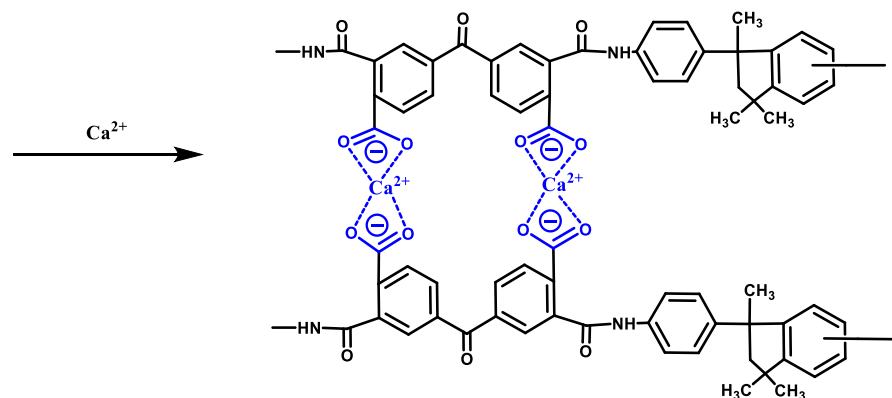
Ca²⁺离子络合交联聚酰亚胺基膜

碱水解 + 金属离子络合交联

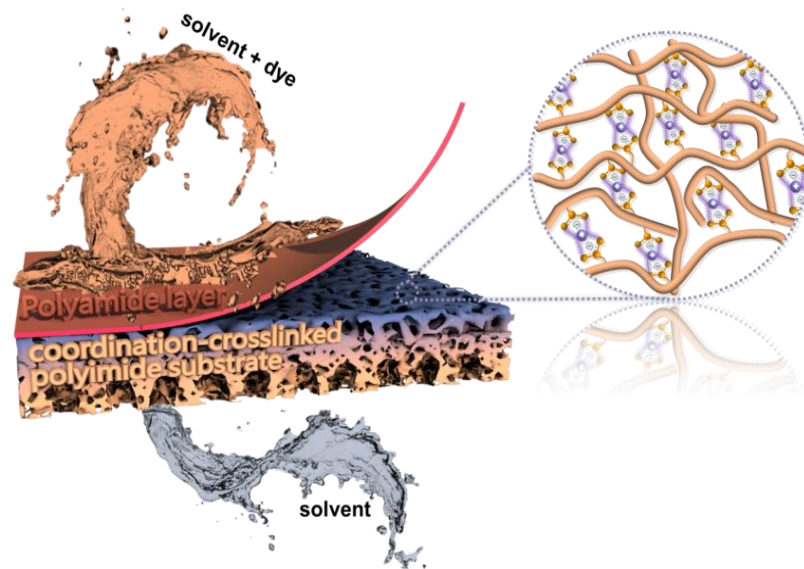
① 碱水解可控优化基膜亲水性和孔径



② 离子络合交联提升基膜耐溶剂性



Original PI
Alkali-modified PI
Ca²⁺-crosslinked PI
Acid-treated PI

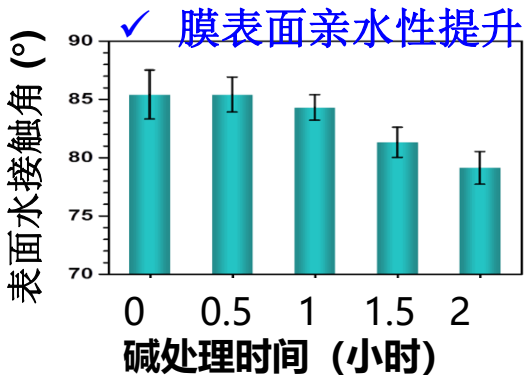
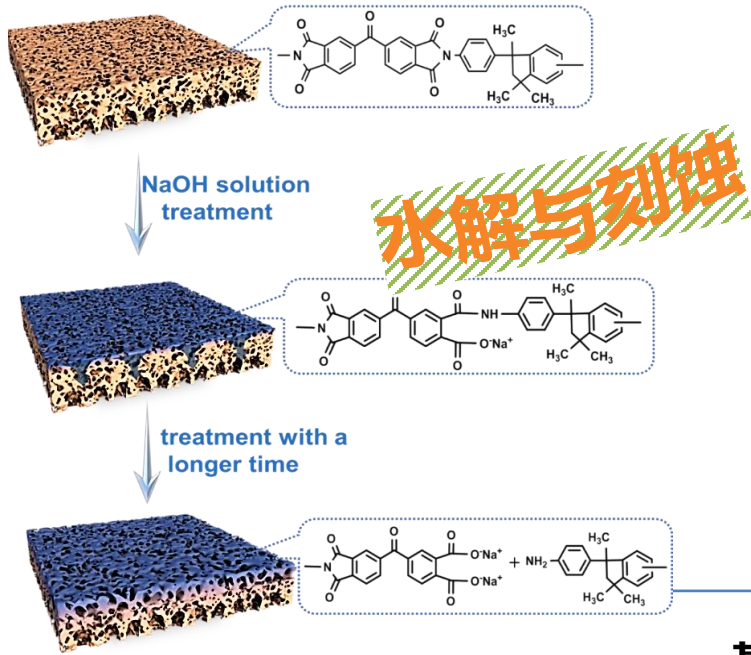


Chem. Eng. J. 427, 130941 (2022).

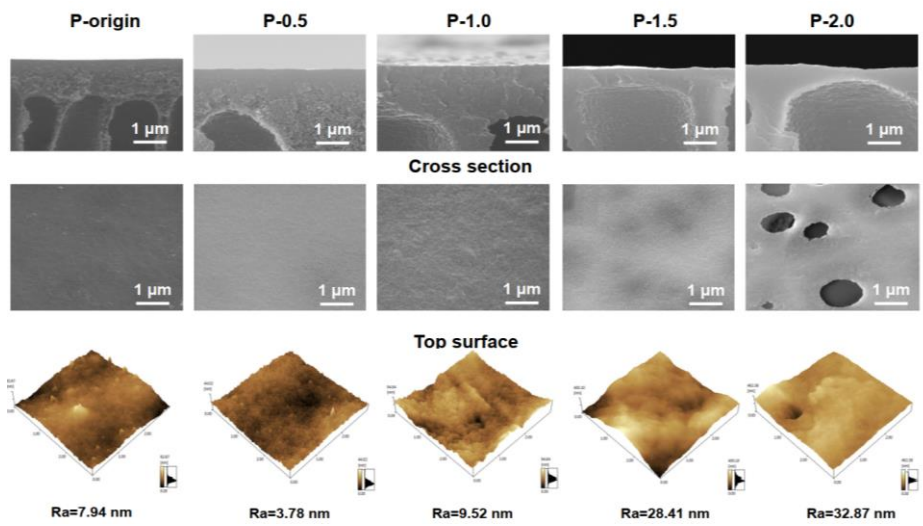
基膜性能优化

Ca²⁺离子络合交联聚酰亚胺基膜

碱凝固浴时间对基膜的影响



- 酰亚胺基团含量下降，酰胺基团含量增加
- 分子量减少，失重量增加



基膜	孔隙率 (%)	MWCO (kDa)	平均孔径 (nm)	纯水通量 (LMH/bar)	凝胶含量 (%)
P-origin	71.9	24	5.36	86.2	0
P-0.5	73.5	65	9.83	178.8	89.2
P-1.0	75.7	80	11.11	225.1	98.3
P-1.5	80.1	289	18.17	278.2	100
P-2.0	81.3	3202	38.81	350.4	100

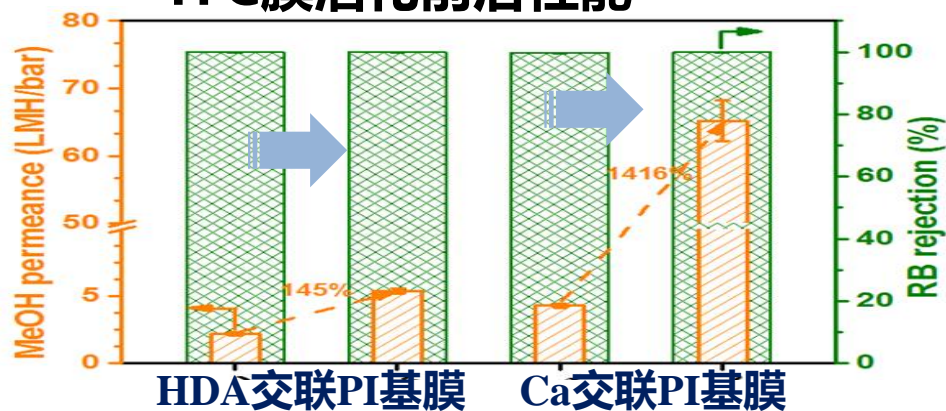
基膜性能优化

DMF活化影响

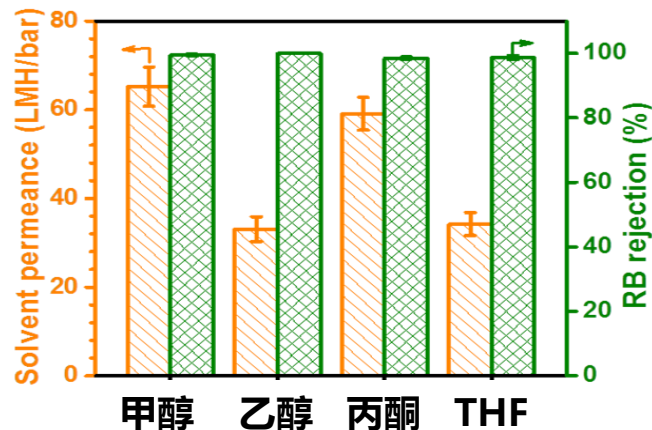


✓ 溶胀与溶解PA层，降低传质阻力

TFC膜活化前后性能



不同溶剂体系

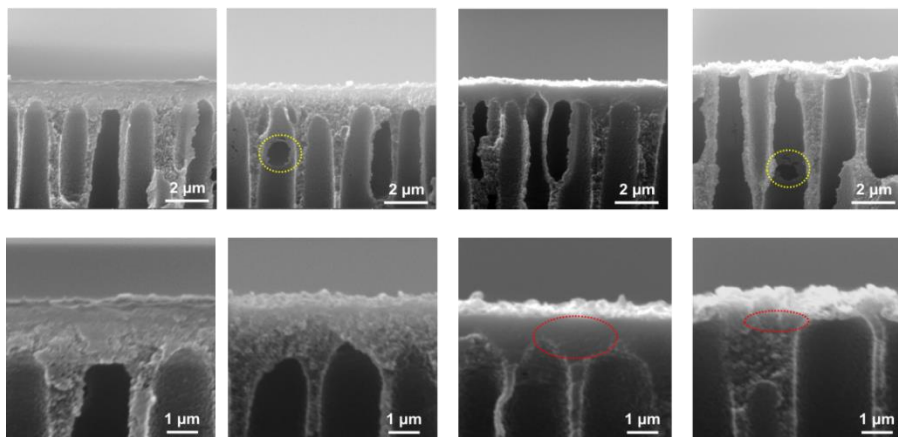


活化前

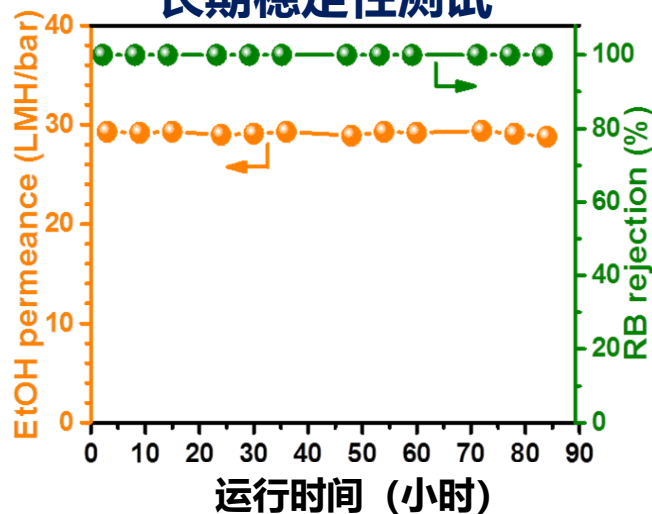
活化后

活化前

活化后



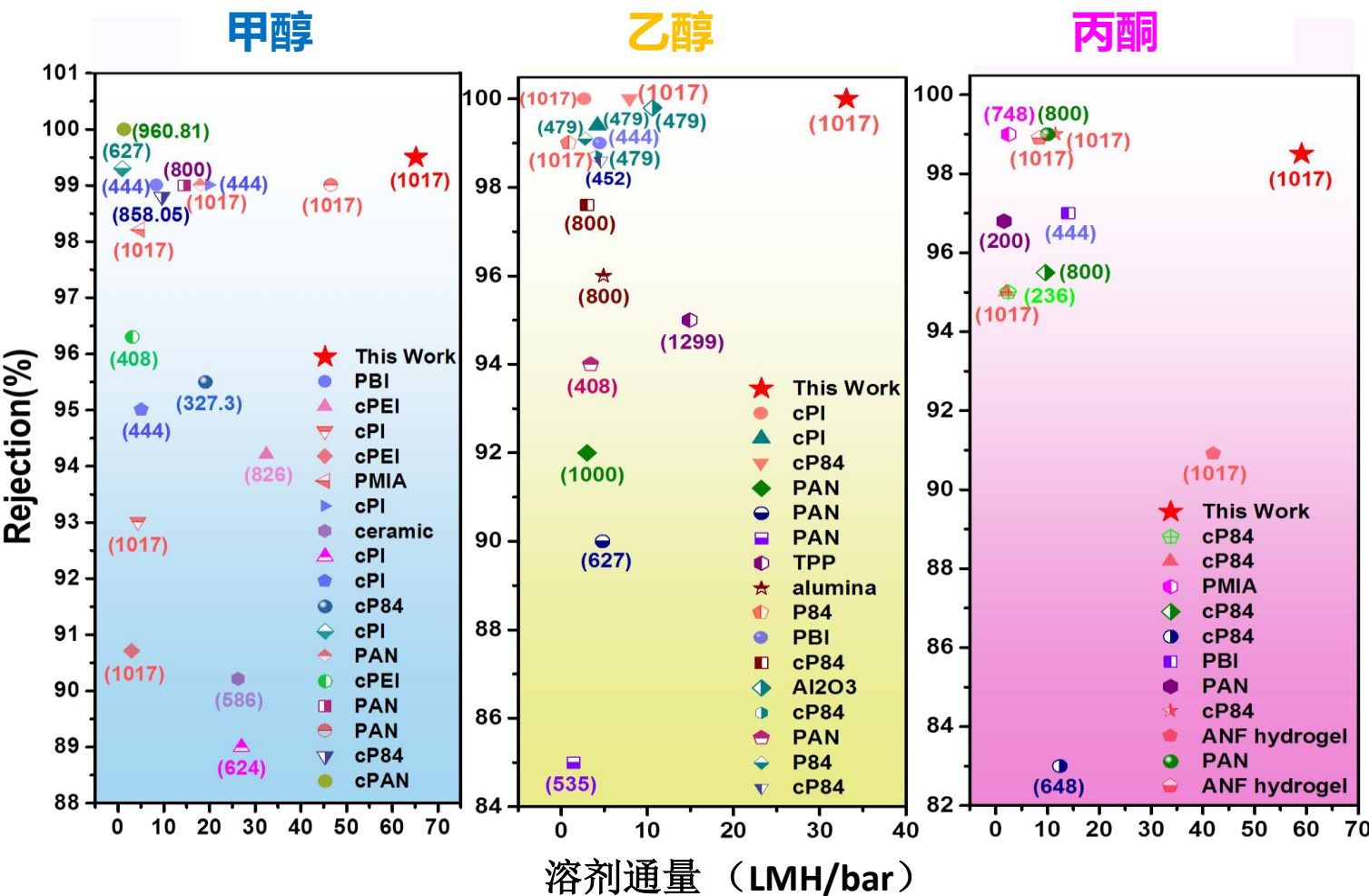
长期稳定性测试



基膜性能优化

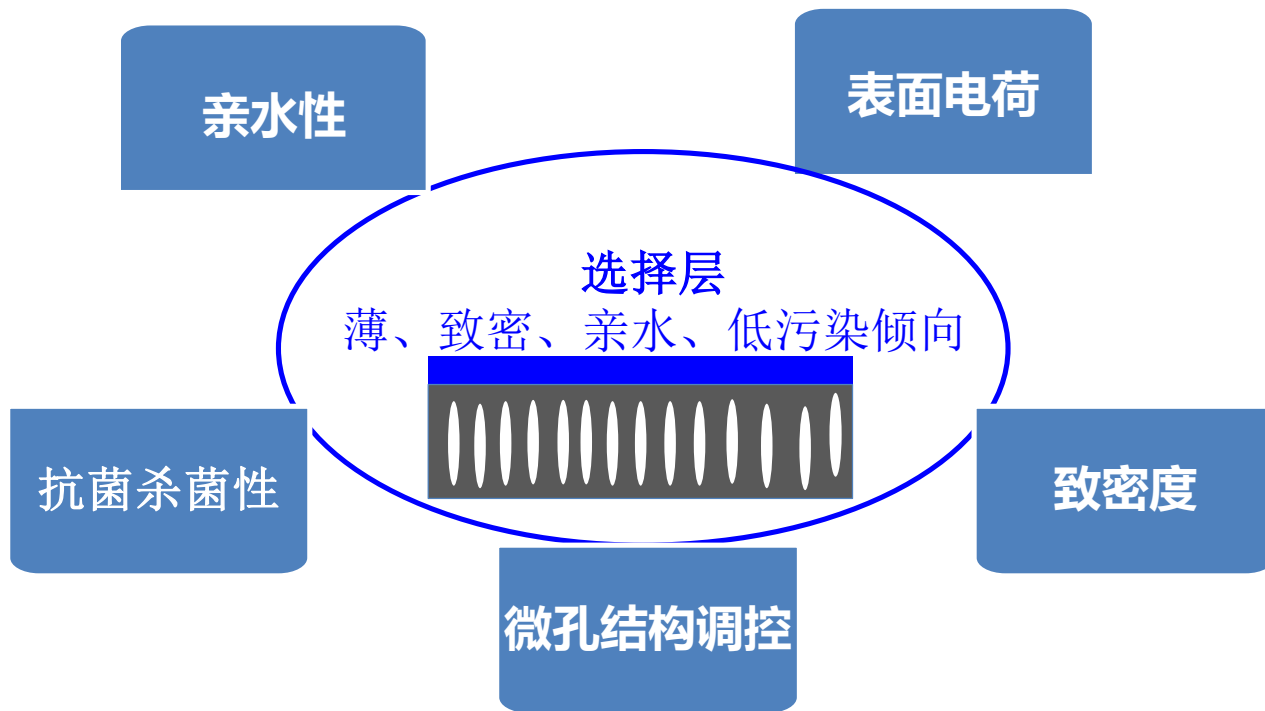
Ca²⁺离子络合交联聚酰亚胺基膜

聚合物基TFC膜OSN性能对比

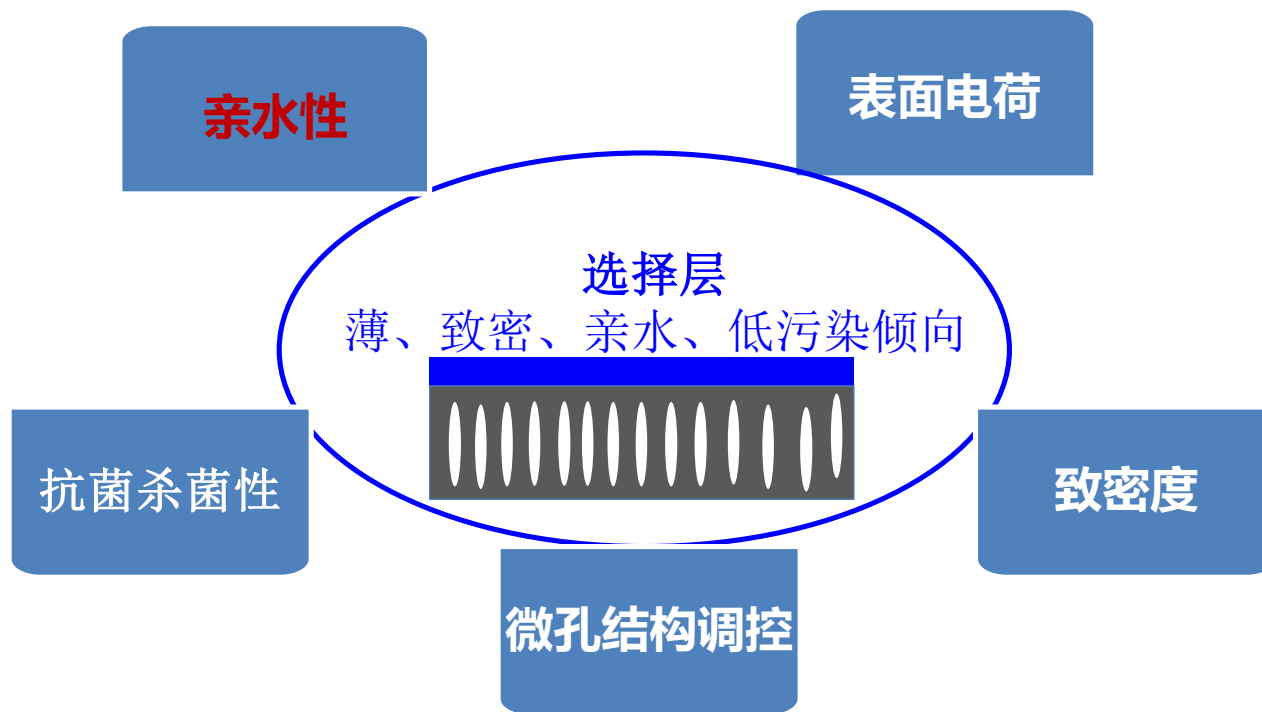


✓基膜适宜的微观形貌、较好的亲水性、优异的耐溶剂性能和后续适当的溶剂活化的综合作用

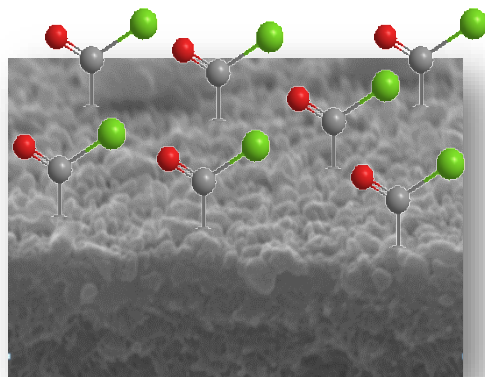
选择层改性



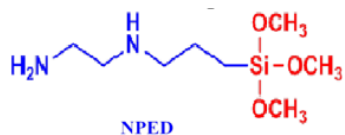
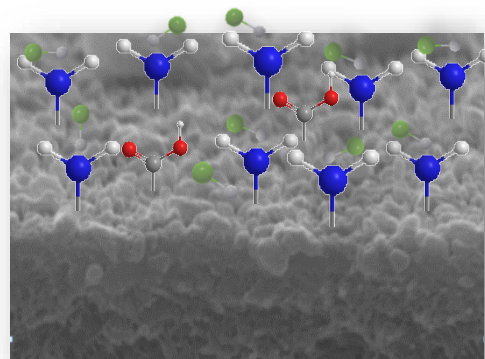
选择层改性



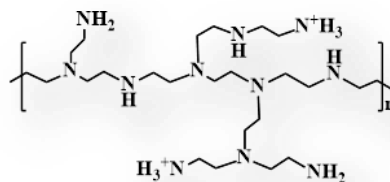
膜表面亲水改性



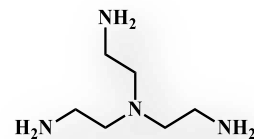
亲水性单体
/ 表面改性



氨基有机硅氧烷
(NPED)



聚乙烯亚胺 (PEI)



多氨基单体
(TAEA)

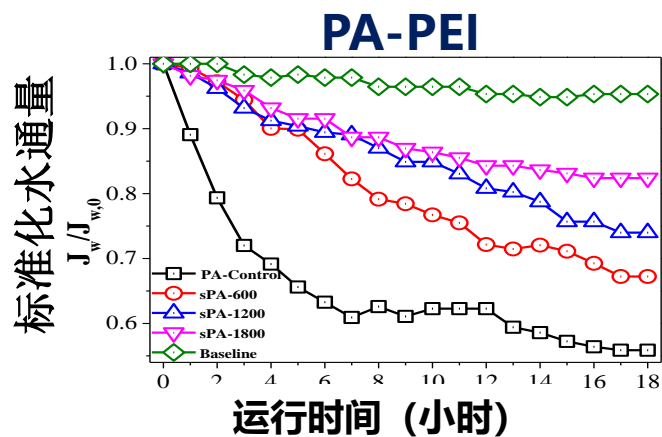
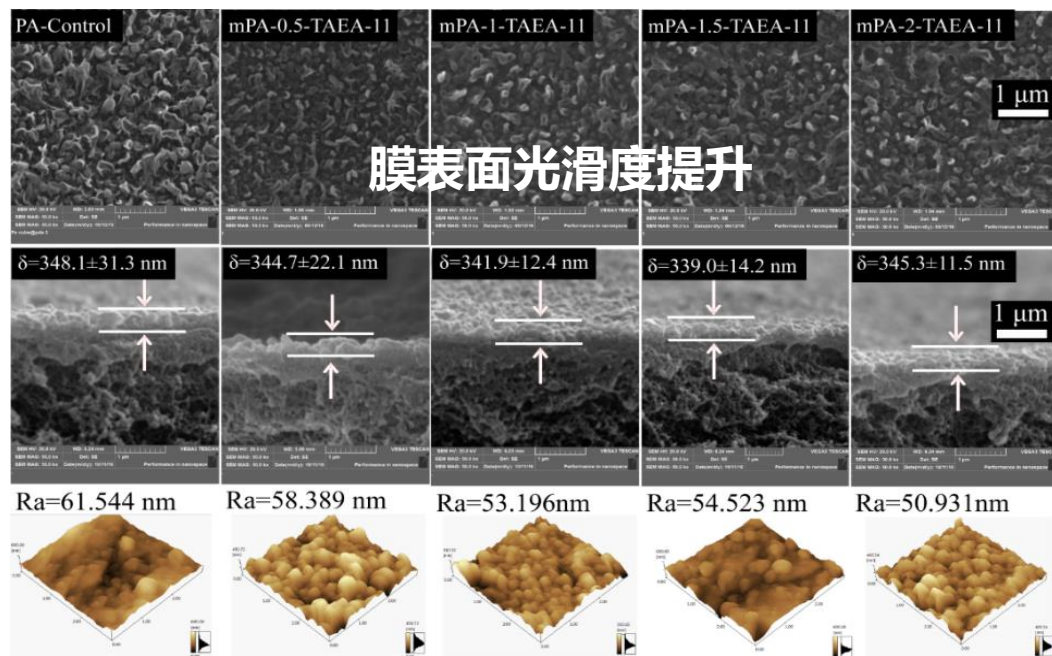
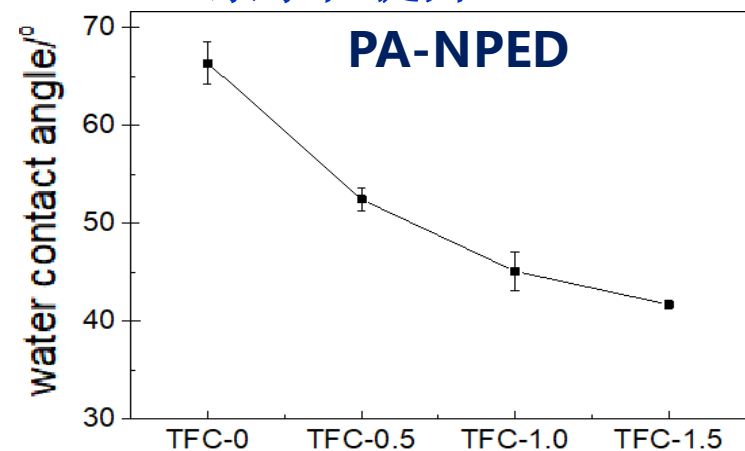
S. Xiong et al, JMS, 2016, 520, 400

L. Shen, et al, JMS, 2017, 534, 46.

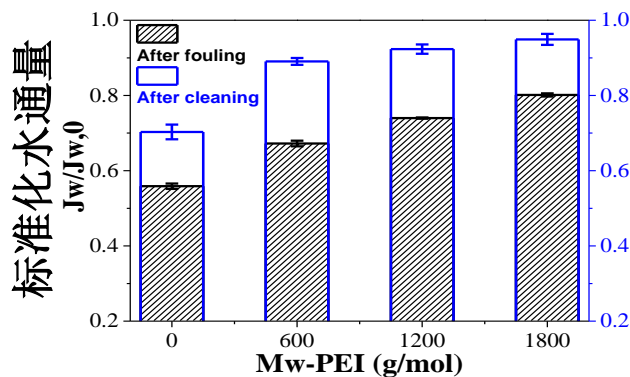
L. Shen, et al, Chem Eng. Sci. 2018, 178, 82.

膜表面亲水改性

✓ 亲水性提升



抗污染性能

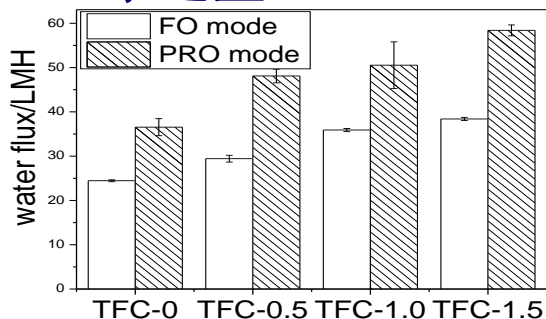


- ✓ 亲水性提升
- ✓ 表面粗糙度降低
- ✓ 表面负电荷降低
- ✓ 减少的 Ca^{2+} 配位位点 ($-\text{COO}-$)

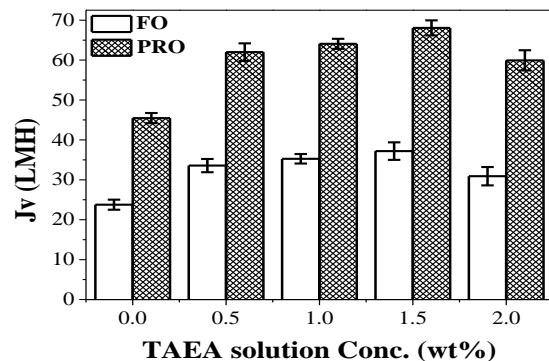
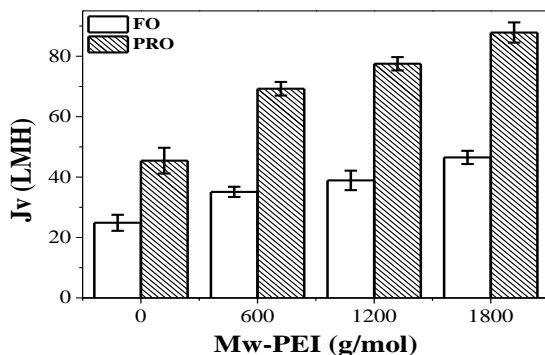
* 料液: 250 ppm 海藻酸钠合成水溶液; 汲取液: 2M NaCl 溶液; $22.5 \pm 0.5^\circ\text{C}$

Hydrophilic modification

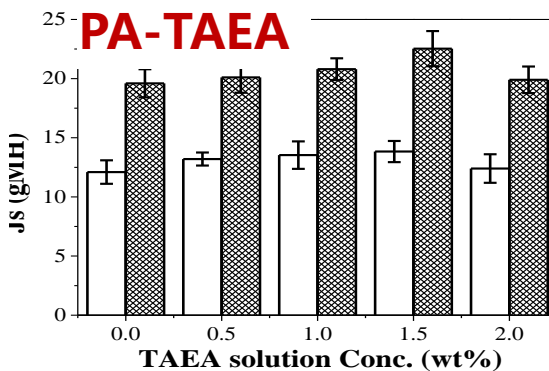
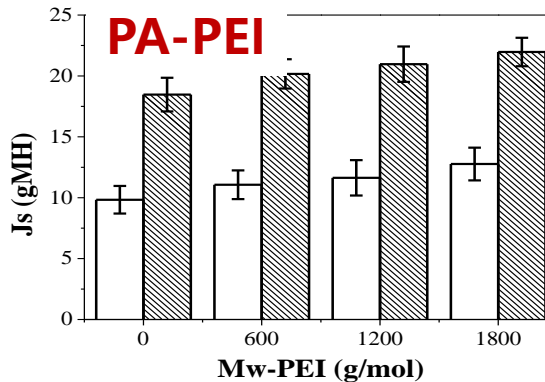
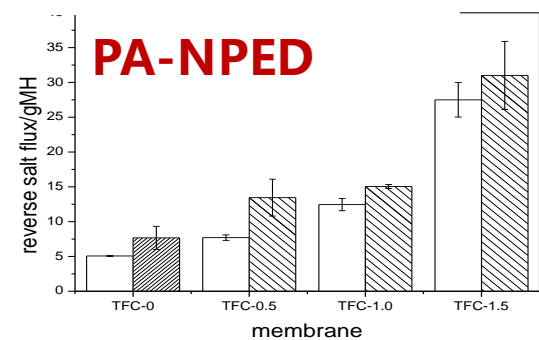
水通量



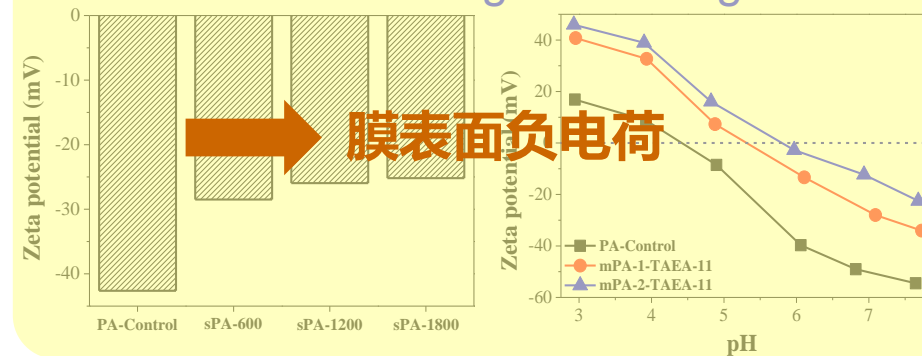
* 料液: 去离子水; 汲取液: 2M Na₂SO₄ 溶液; 22.5 ± 0.5°C



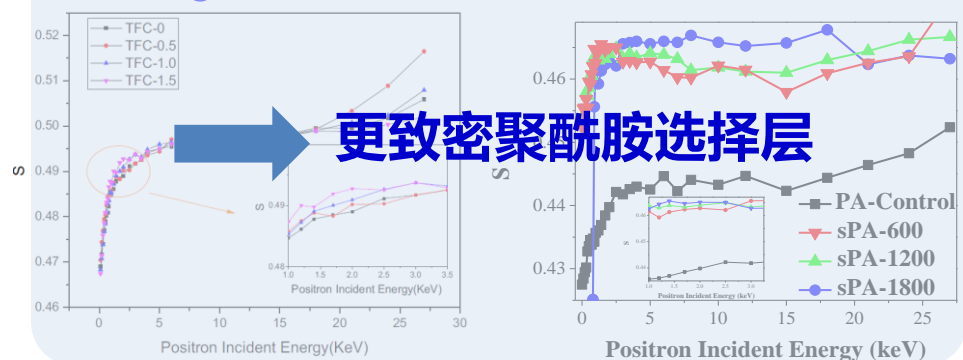
反向盐通量



Less surface negative charge

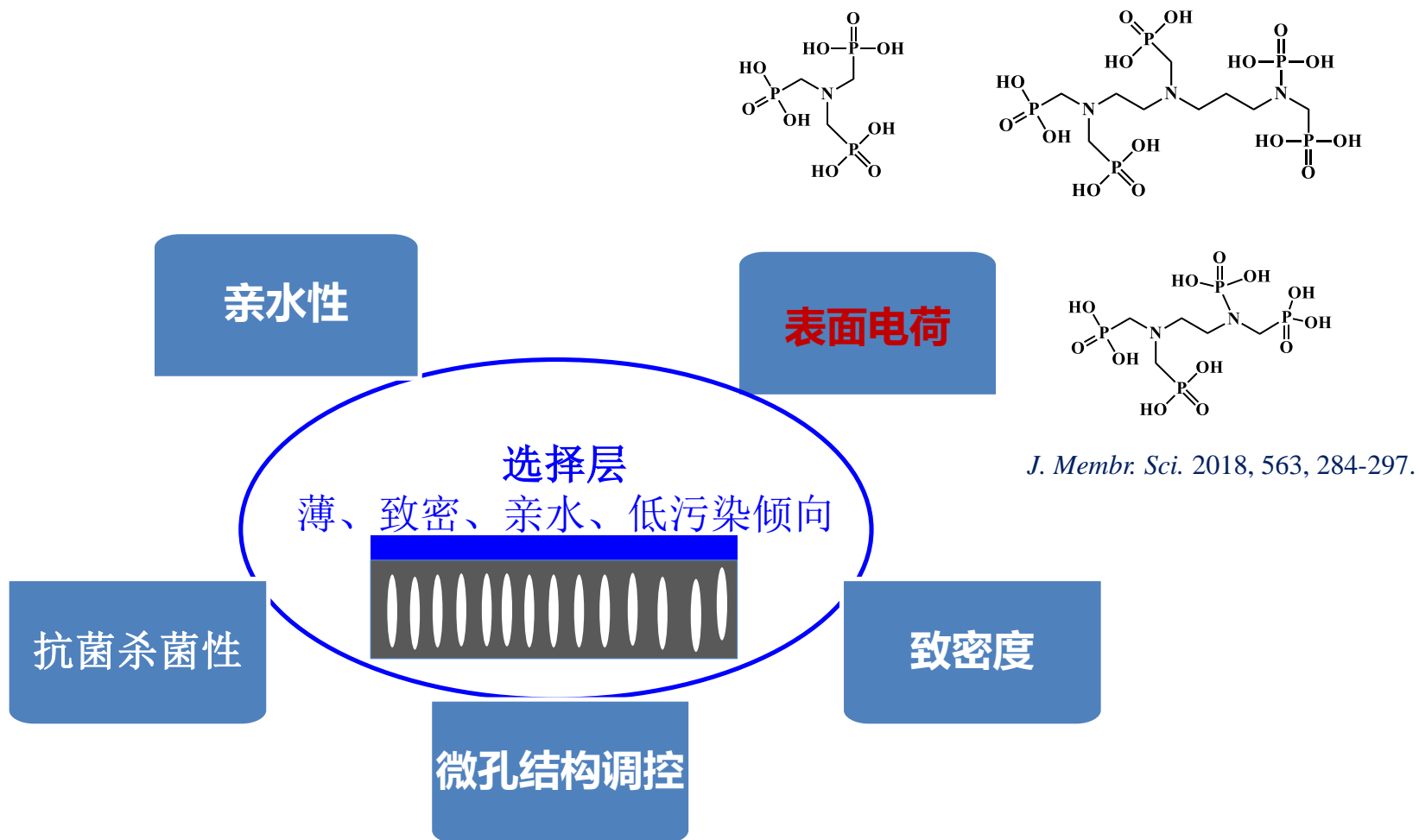


Larger FFV



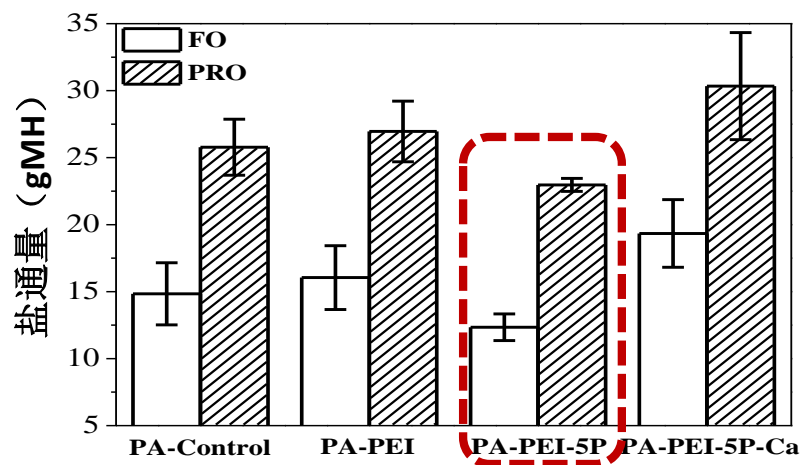
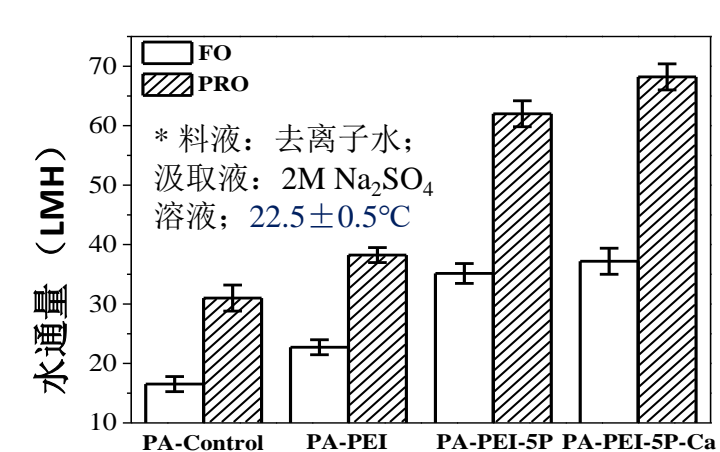
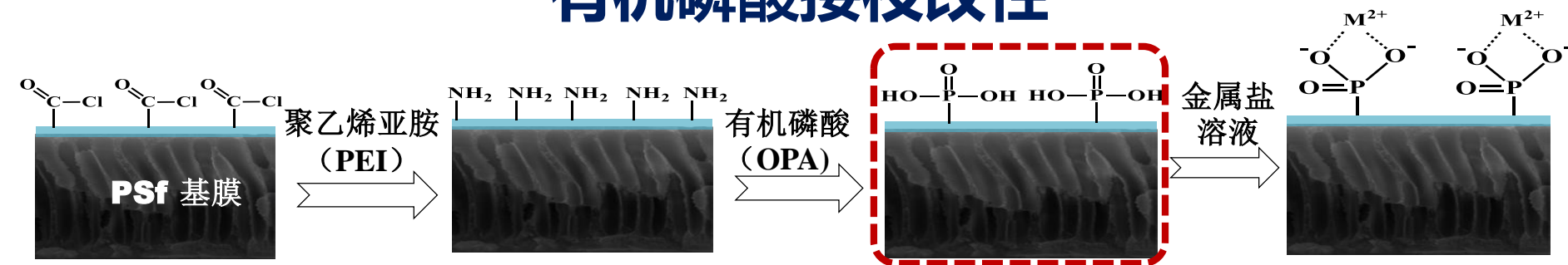
更致密聚酰胺选择层

报告内容

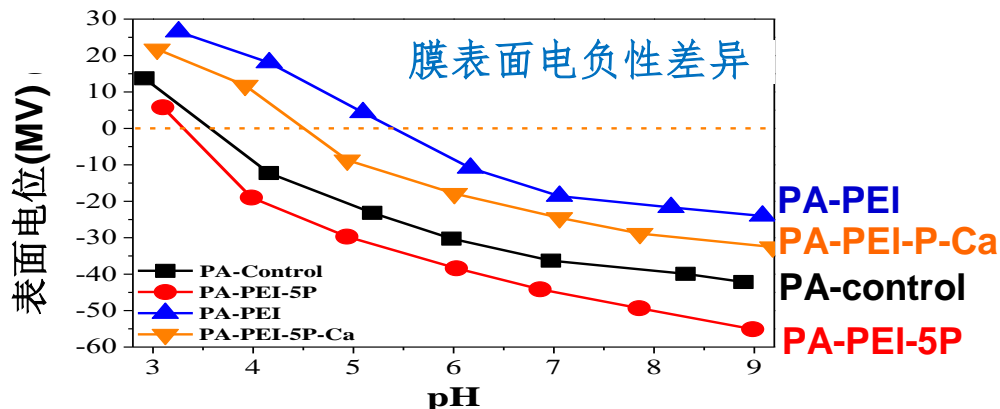
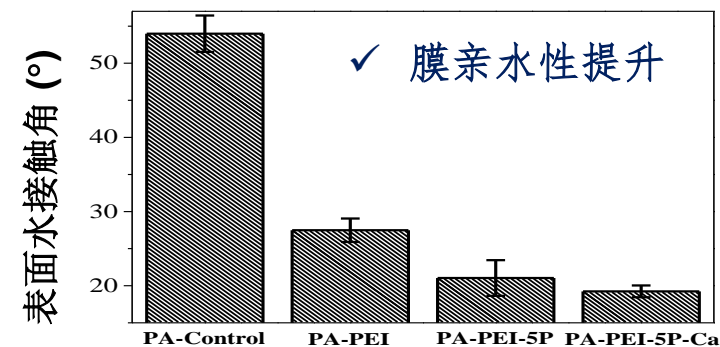


表面电荷改性

有机磷酸接枝改性



L. Shen, et al, *J. Membr. Sci.* 2018, 563, 284.



有机磷酸接枝改性

Figure 1: Chemical structures and growth parameters of FO and PRO strains.

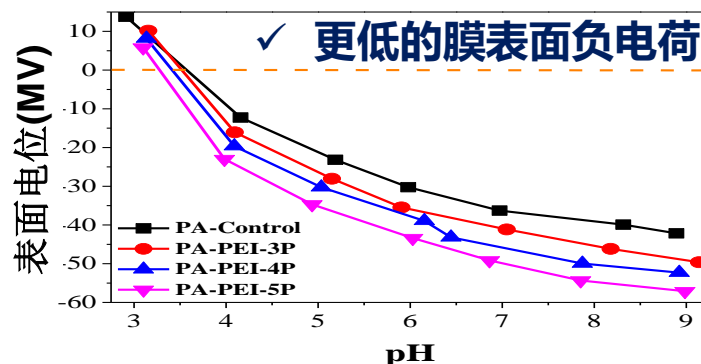
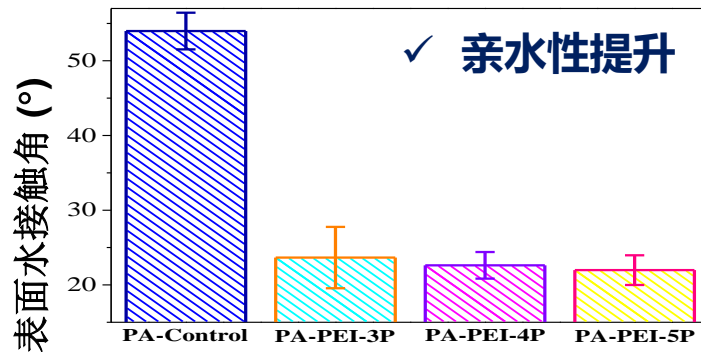
The figure displays the chemical structures of FO (orange), PRO (blue), and a modified FO-PRO (pink) strain. The FO structure is a linear chain with three phosphate groups. The PRO structure is a branched chain with four phosphate groups. The modified FO-PRO structure is a branched chain with five phosphate groups.

The growth parameters for the strains are shown in two bar charts. The top chart shows water flux (LMH) for PA-Control, PA-PEI-3P, PA-PEI-4P, and PA-PEI-5P. The bottom chart shows salt flux (gMH) for the same conditions. In both charts, FO is represented by red bars and PRO by blue bars. The modified FO-PRO is represented by pink bars. The growth parameters are significantly higher for the modified FO-PRO than for the other strains.

Strain	FO (LMH)	PRO (LMH)
PA-Control	~16	~30
PA-PEI-3P	~24	~45
PA-PEI-4P	~27	~50
PA-PEI-5P	~34	~61

Strain	FO (gMH)	PRO (gMH)
PA-Control	~14	~25
PA-PEI-3P	~13	~24
PA-PEI-4P	~12	~23
PA-PEI-5P	~12	~23

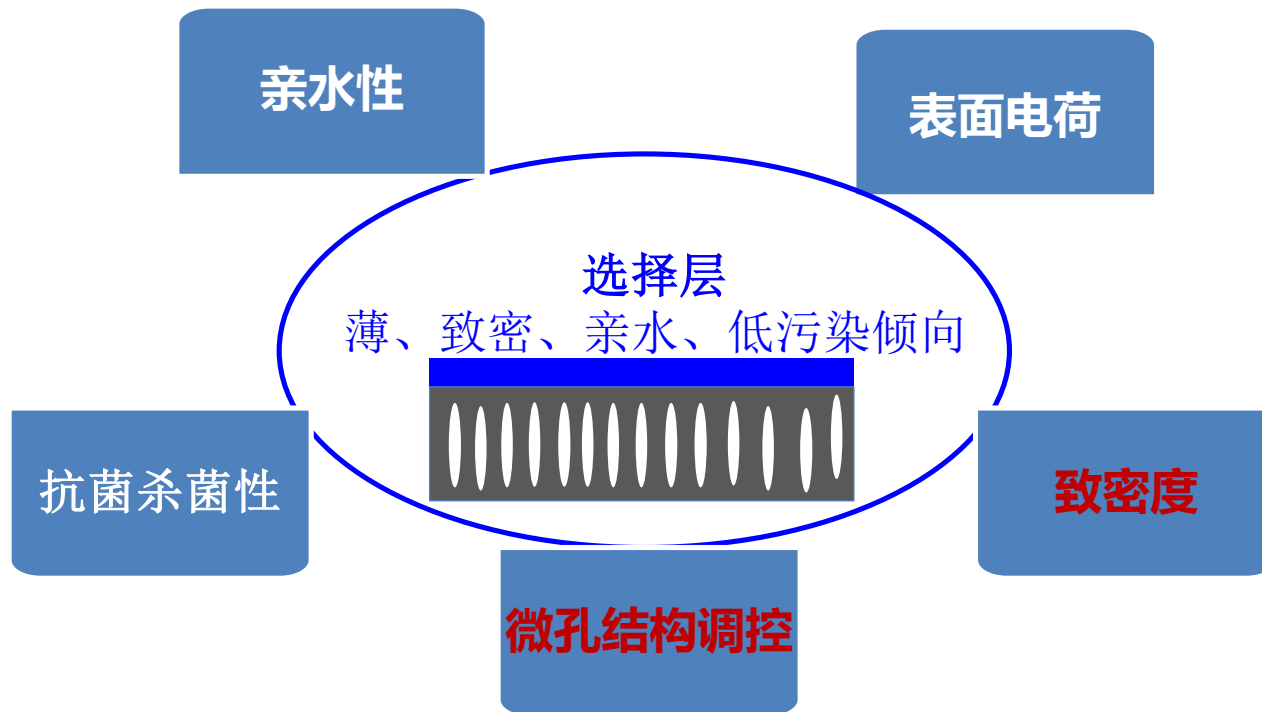
Testing time (h)	PA-Control	PA-PEI	PA-PEI-P	PA-PEI-P-Ca ²⁺	Baseline
0	1.00	1.00	1.00	1.00	1.00
2	0.92	0.95	0.97	0.94	1.00
4	0.84	0.94	0.96	0.90	1.00
6	0.81	0.91	0.94	0.89	1.00
8	0.78	0.89	0.93	0.86	0.99
10	0.75	0.85	0.91	0.83	0.99
12	0.74	0.83	0.89	0.81	1.00
14	0.71	0.82	0.86	0.79	0.99
16	0.68	0.80	0.84	0.77	0.98
18	0.66	0.80	0.84	0.77	0.98



- ✓ 膜表面亲水性提升
- ✓ 空间位阻效应
- ✓ Ca^{2+} 配位位点 ($-\text{COO}-$)减少
- ✓ 增加/减少的表面负电荷

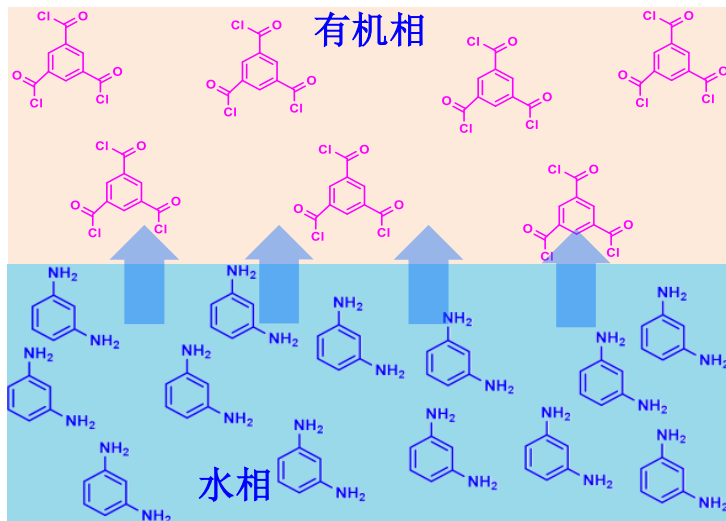
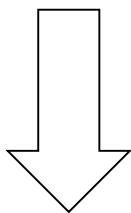
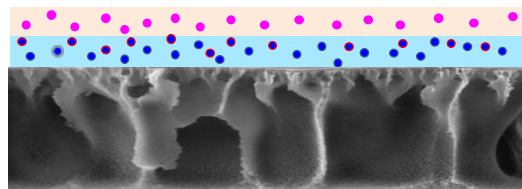
料液：250 ppm SA 合成废水或本地湖水；汲取液：2 M NaCl 溶液；FO 模式：150 rpm, 0.3L/min；22.5 ± 0.5 °C

报告内容

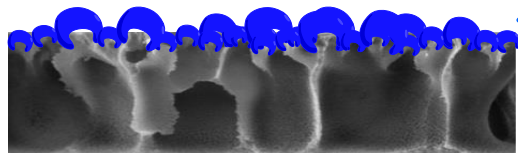


PA层微孔结构调控

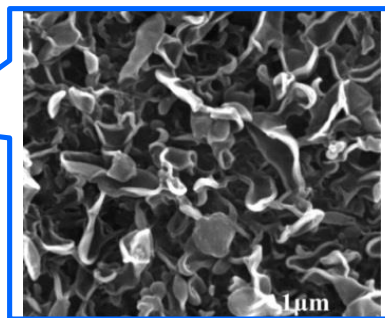
界面聚合过程



- 水相胺单体向有机相的迁移决定了IP反应速率
- 自抑制的反应 (“Marangoni” 效应)



TFC 复合膜

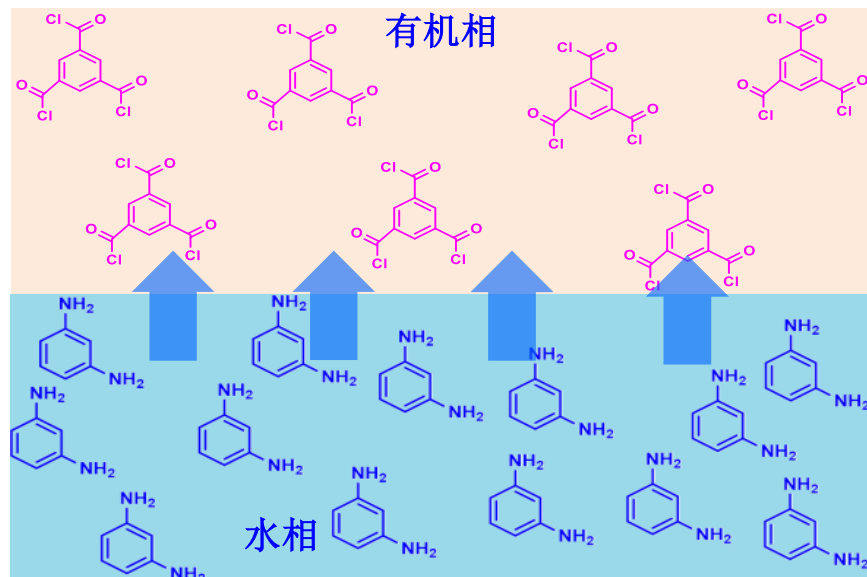


聚酰胺选择层

- “表面粗糙的脊骨形貌
- 不易控制聚酰胺层的微观结构

PA层微孔结构调控

调控界面聚合过程

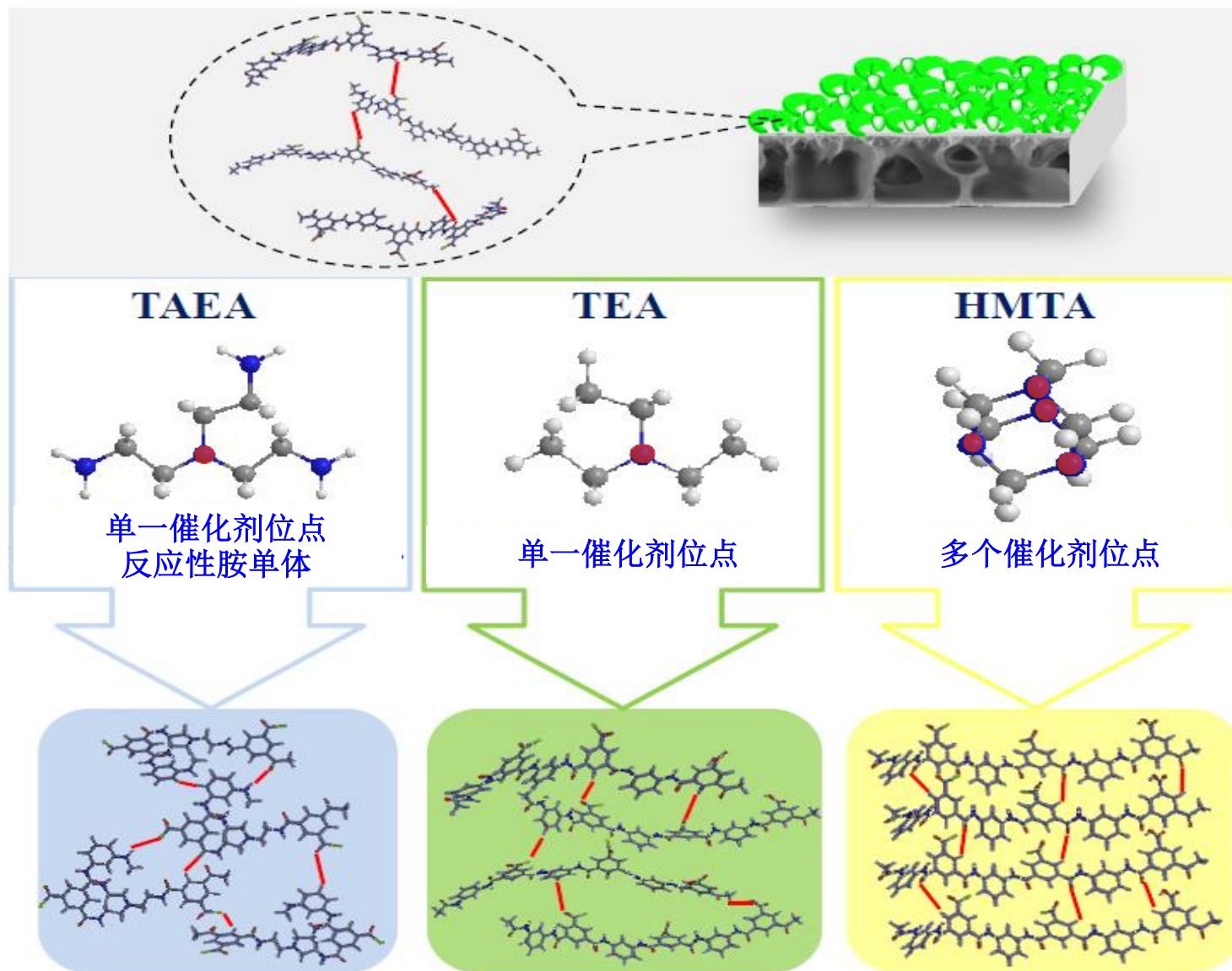


- 如何增高反应程度？
- 优化膜的微观结构？

1. 叔胺调控界面聚合(吸收副产物HCl)
2. 基膜中引入 $p\text{-TiO}_2$ 以优化PA选择层
3. 超声辅助的界面聚合
4. 使用含环糊精结构的反应单体

PA层致密度调控

叔胺调控的 界面聚合

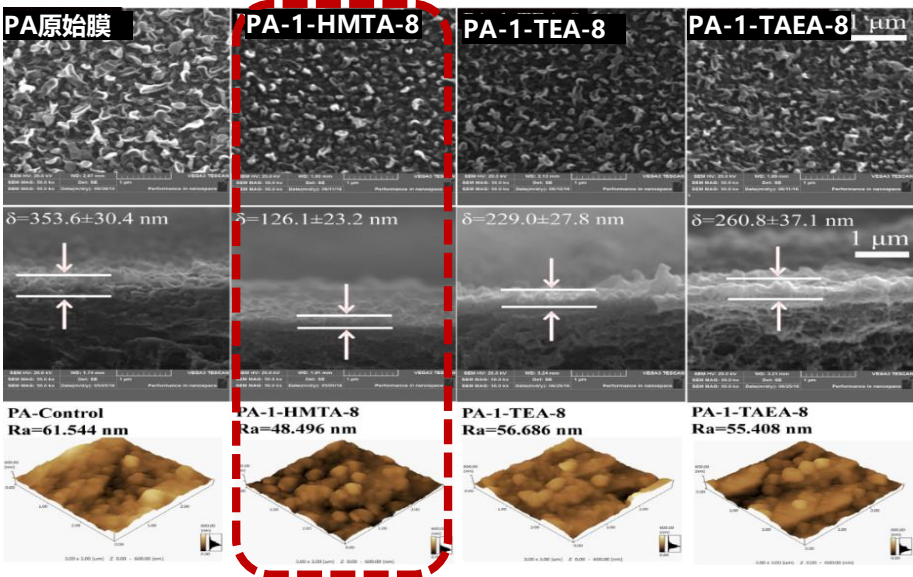


L. Shen, et al, *J. Membr. Sci.* 2017, 537, 186–201.

L. Shen, et al, *Advanced Composites Hybrid Materials*, 2019, 2(1), 51-69.

PA层致密度调控

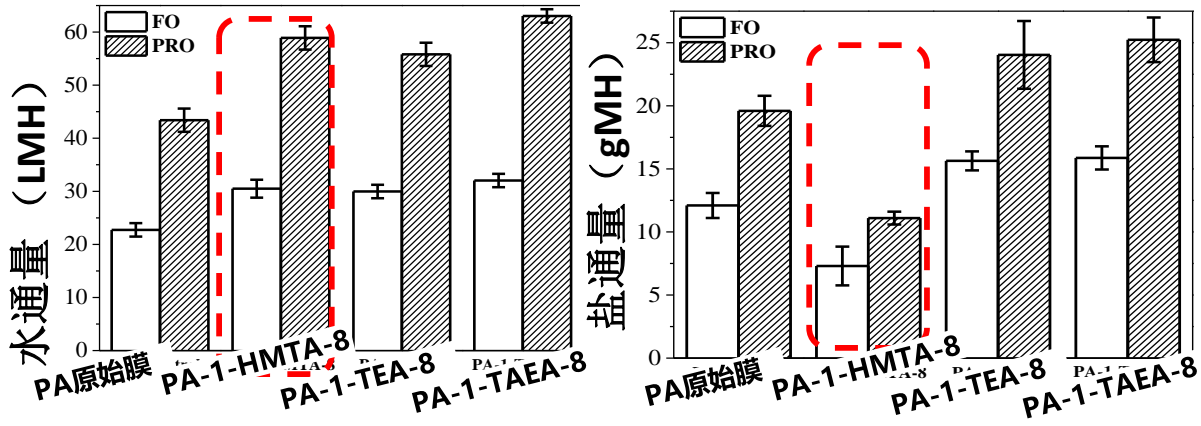
复合膜形貌



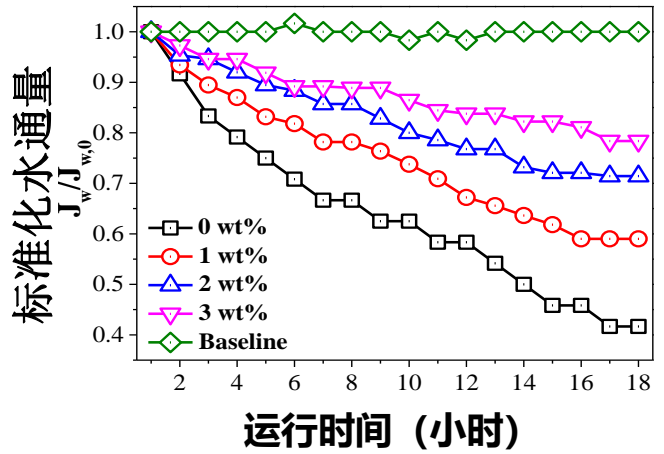
叔胺调控的界面聚合

复合膜	交联度(%)
PA-Control	15.82
PA-1-TEA-8	24.69
PA-1-TAEA-8	/
PA-1-HMTA-8	40.00
PA-2-HMTA-8	65.49
PA-3-HMTA-8	76.47

FO性能



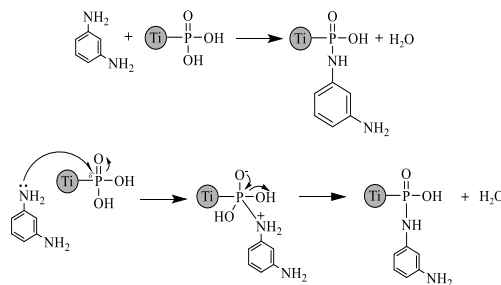
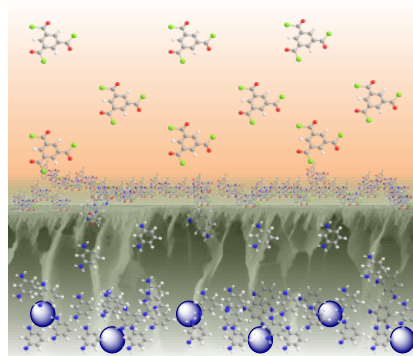
抗污染性能



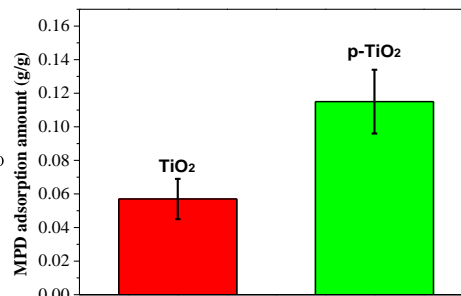
* 料液: 去离子水; 汲取液: 2 M NaCl 溶液; 22.5 °C

PA层致密度调控

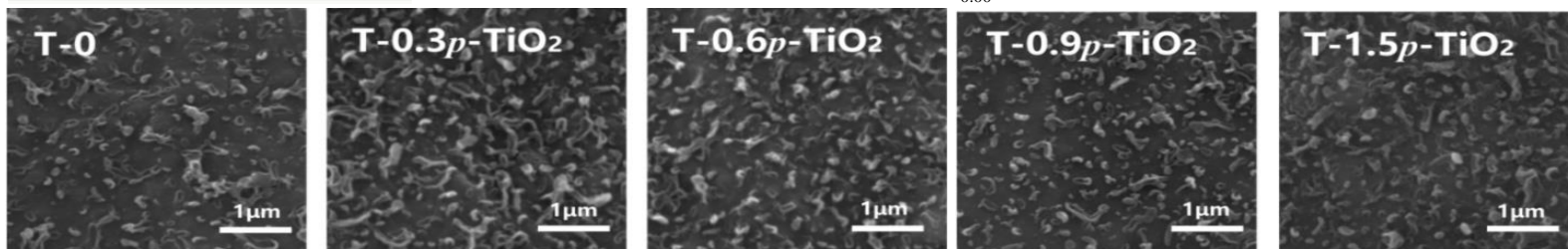
基膜中磷酸化TiO₂的引入对选择层的调控



✓ 水相单体吸附增多

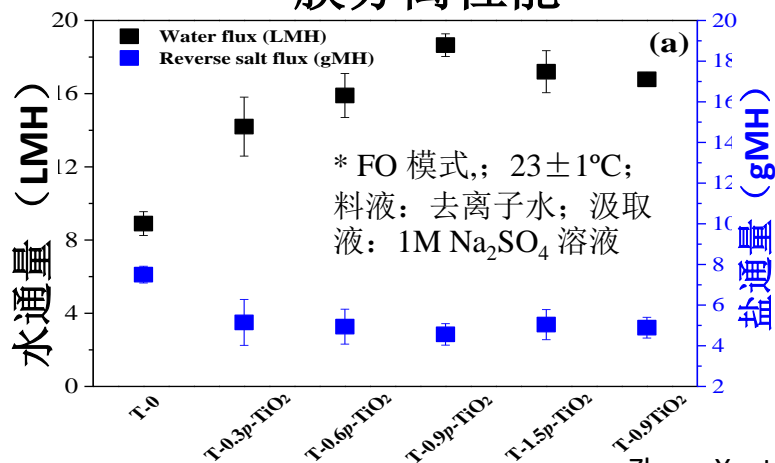


- 促进 MPD 在基膜上均匀吸附
- 限制MPD在界面聚合过程中向有机相迁移

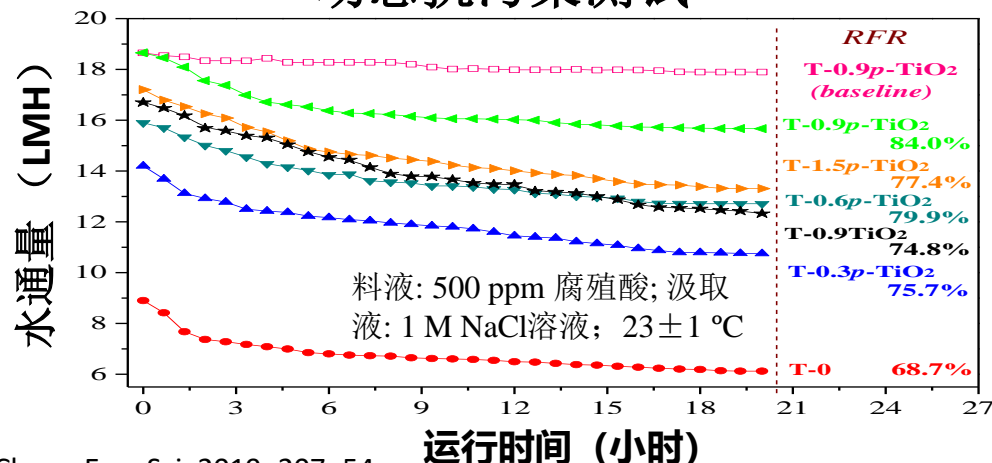


✓ 选择层交联度提高

膜分离性能



动态抗污染测试



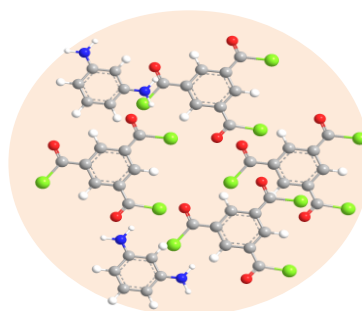
PA层微孔结构调控

传统的界面聚合反应

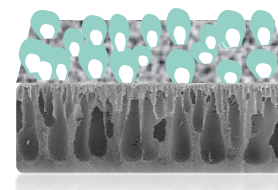
狭窄的混合界面
与聚合区域



单体混合有限

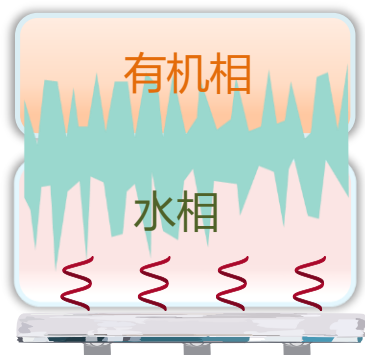


PA层较薄、
表面较粗糙、
自由体积较小

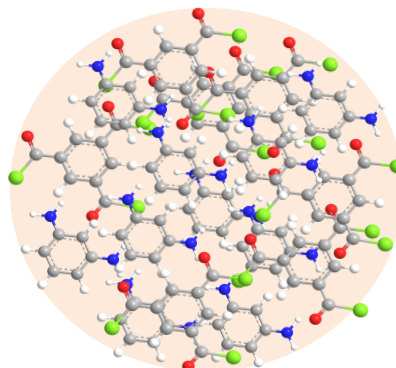


超声辅助的界面聚合反应

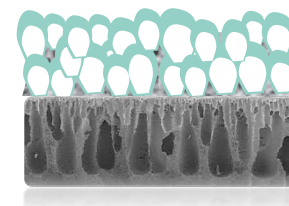
较大的混合界面
与聚合区域



高效的单体混合

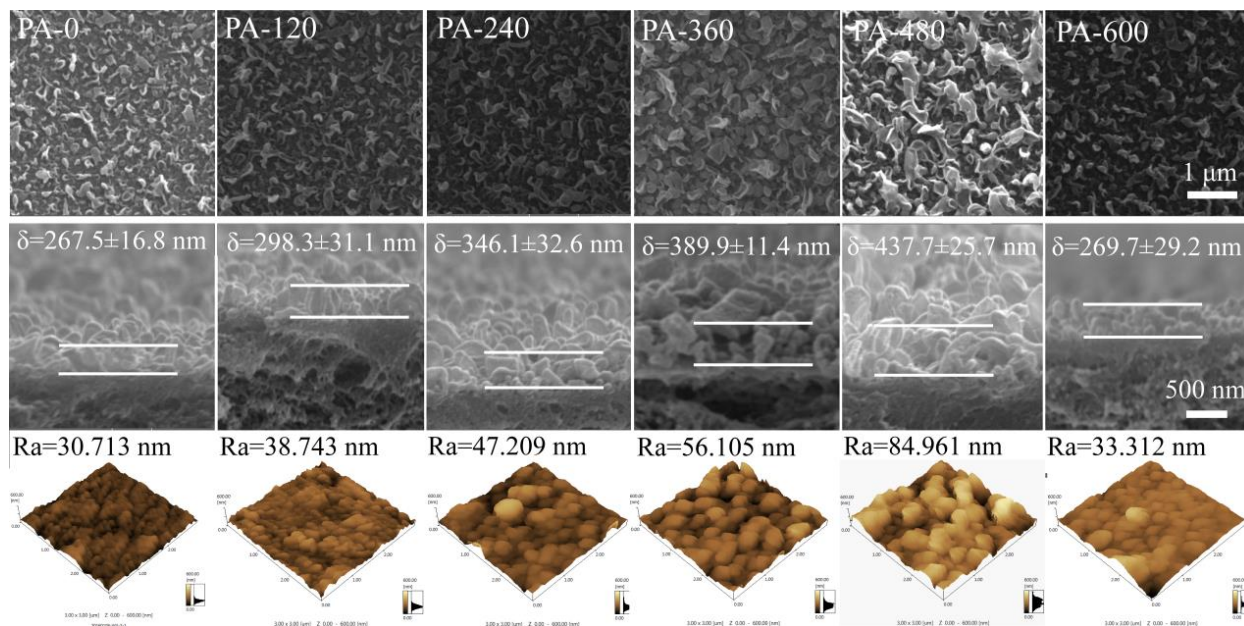


PA层较厚、
表面较粗糙
自由体积较大



PA层微孔结构调控

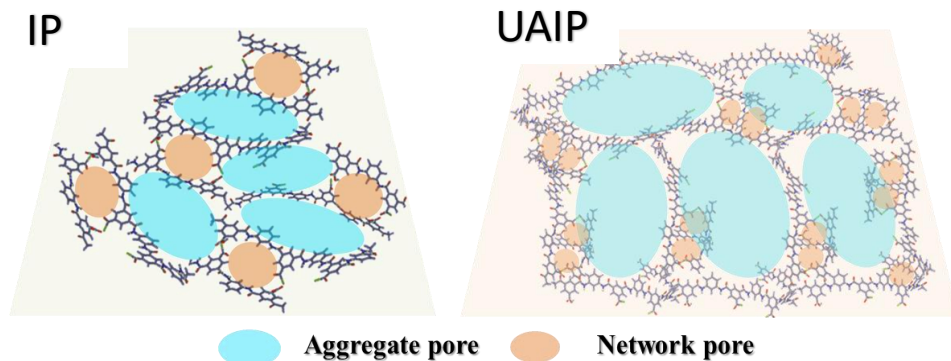
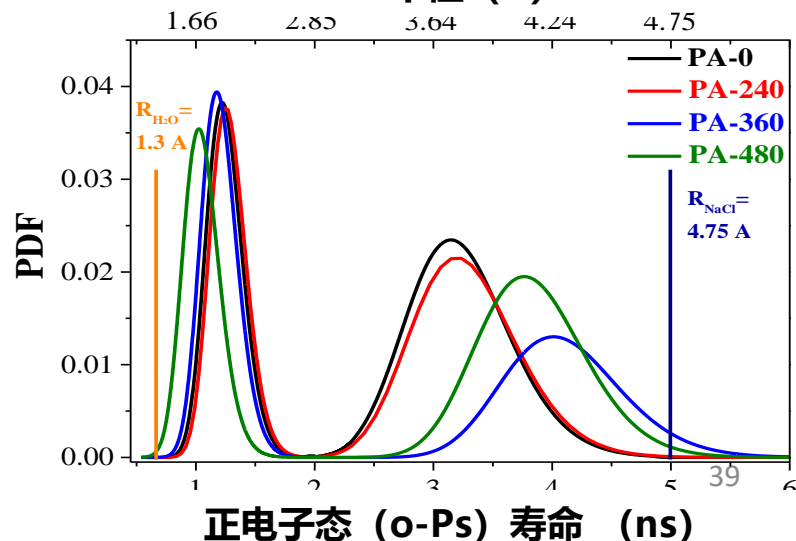
超声辅助的界面聚合



- ✓ 选择层更厚
- ✓ 表面更致密更粗糙
- ✓ 交联度提升

正电子态 (o-Ps) 寿命分布

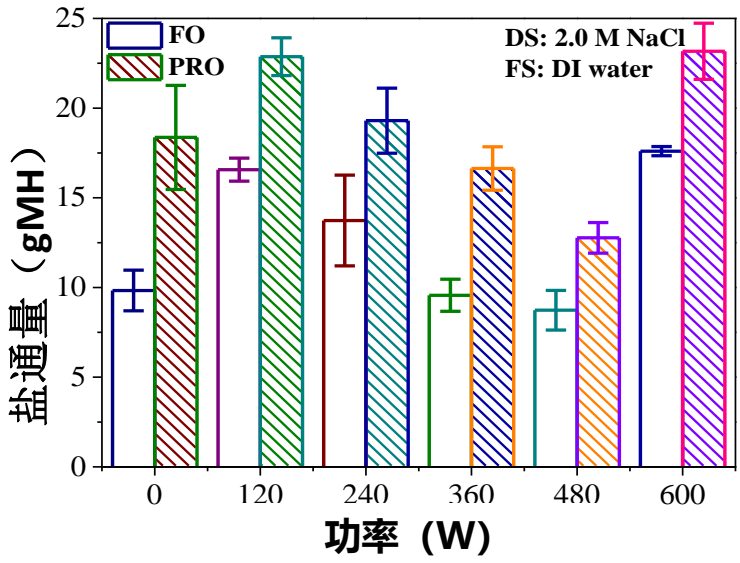
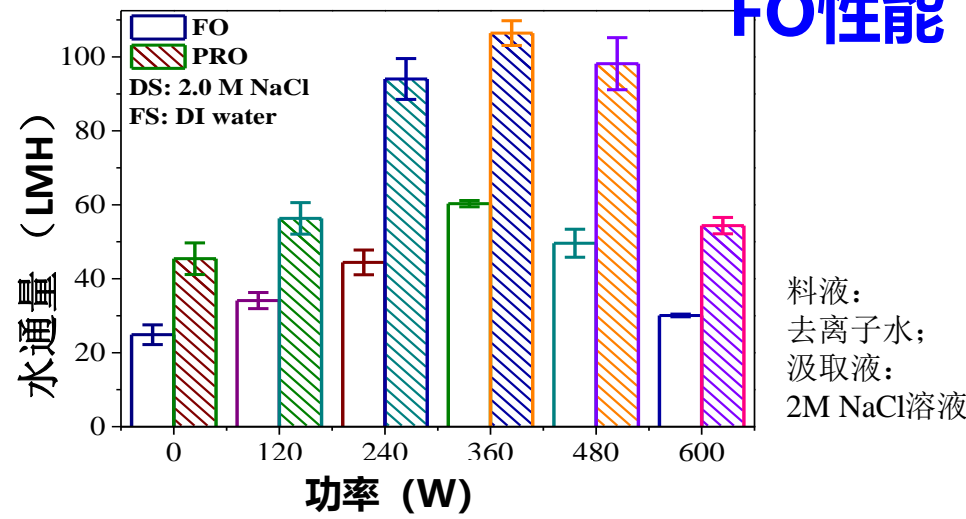
半径 (Å)



PA层微孔结构调控

超声辅助的界面聚合

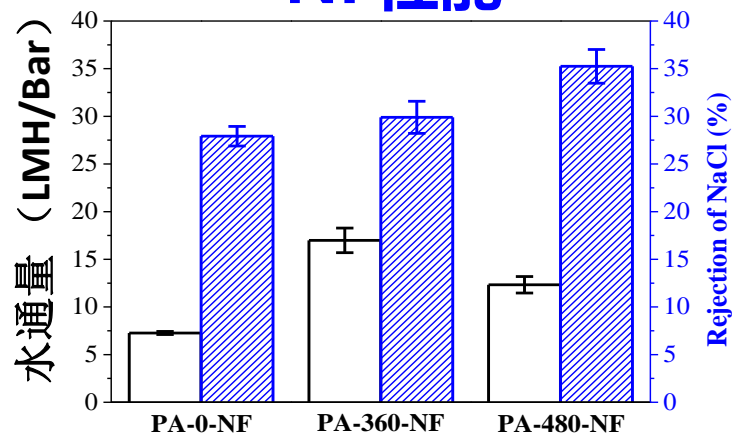
FO性能



RO性能

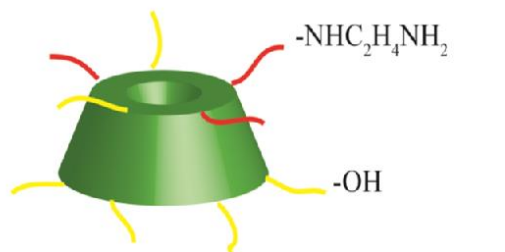
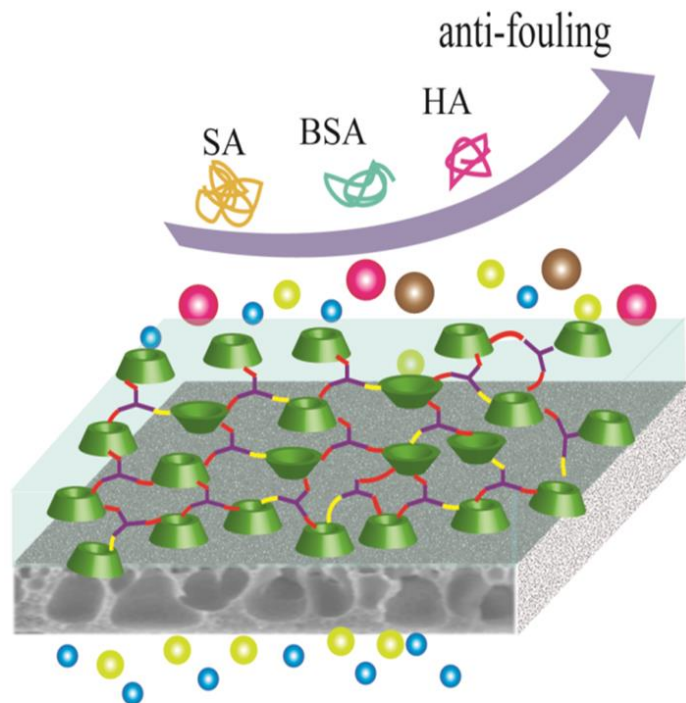
膜	A ^a , LMH/Bar	B ^b , LMH	截盐率 R _s , %	B/A, Bar
PA-0	1.99±0.10	0.18±0.05	94.72±1.05	0.09
PA-120	2.26±0.11	0.22±0.04	93.96±1.18	0.11
PA-240	2.67±0.10	0.26±0.05	94.30±0.82	0.10
PA-360	3.44±0.09	0.23±0.07	95.92±1.05	0.07
PA-480	3.21±0.09	0.18±0.08	96.67±1.43	0.05
PA-600	2.32±0.10	0.35±0.02	91.13±0.87	0.15

NF性能

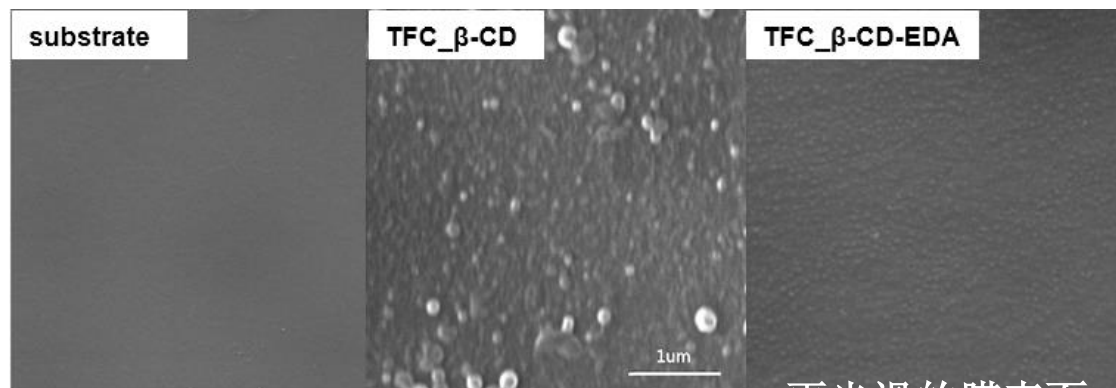
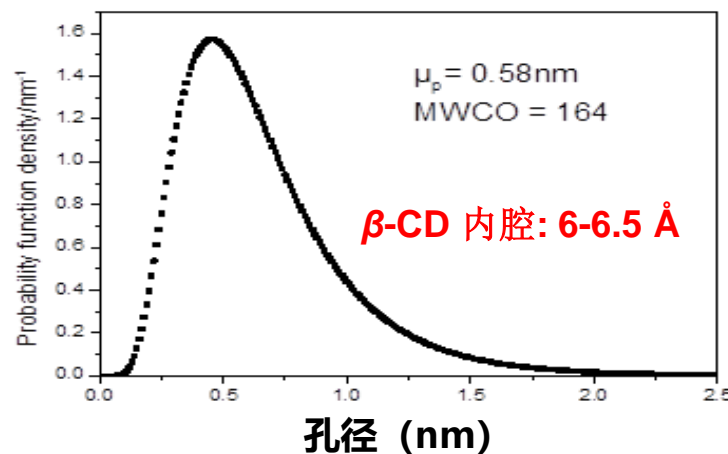


PA层微孔结构调控

乙二胺功能化环糊精(β -CD-EDA)对PA层的改性



孔径分布

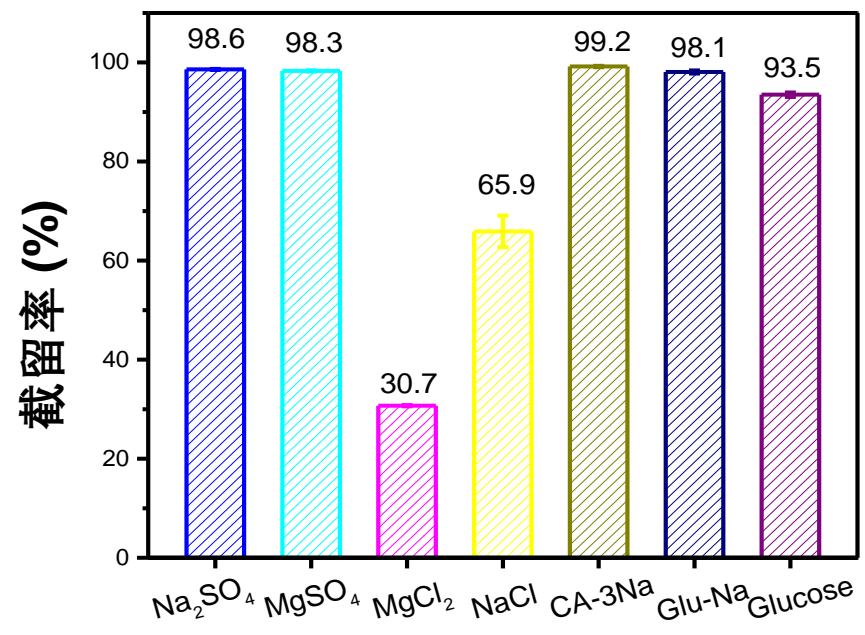
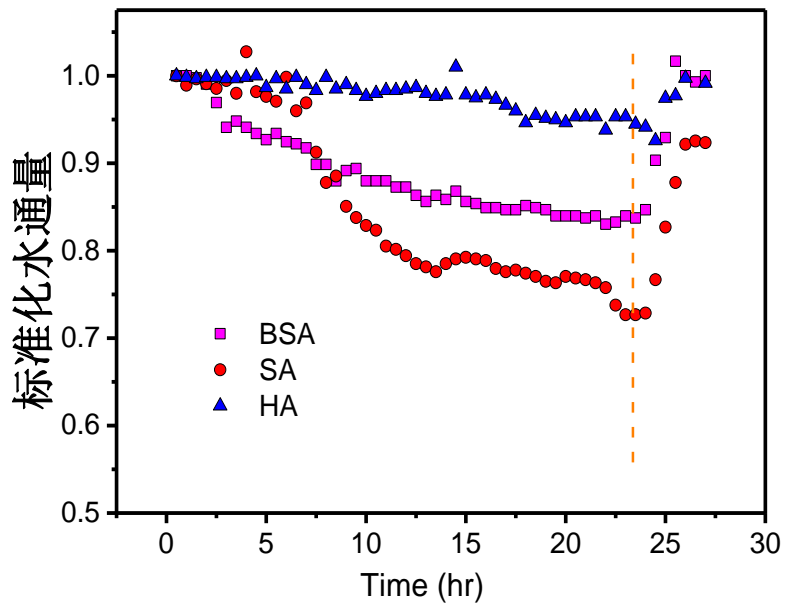


PA层微孔结构调控

乙二胺功能化环糊精(β -CD-EDA)对PA层的改性

CD-EDA对NF膜性能的影响

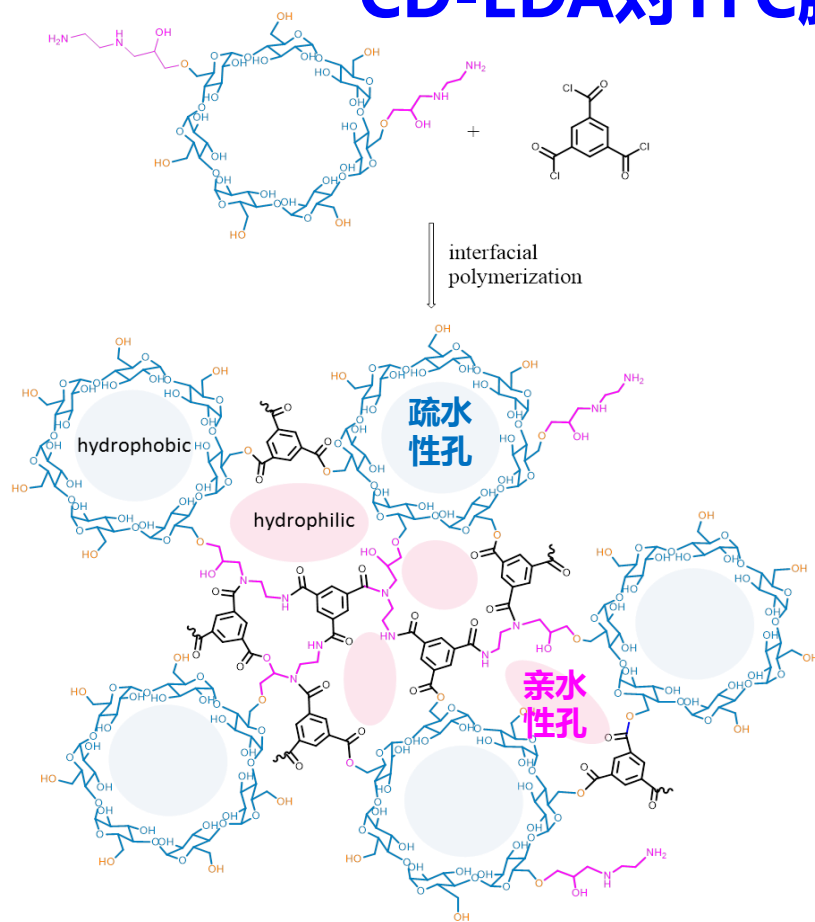
膜	水通量 (LMH/bar)	Na ₂ SO ₄ 截留率 (%)
TFC_β-CD	62.6±0.7	53.7±0.6
TFC_β-CD-EDA	4.4±0.3	98.6±0.1



PA层微孔结构调控

乙二胺功能化环糊精(CD-EDAs)对PA层的改性

CD-EDA对TFC膜选择层孔结构的影响

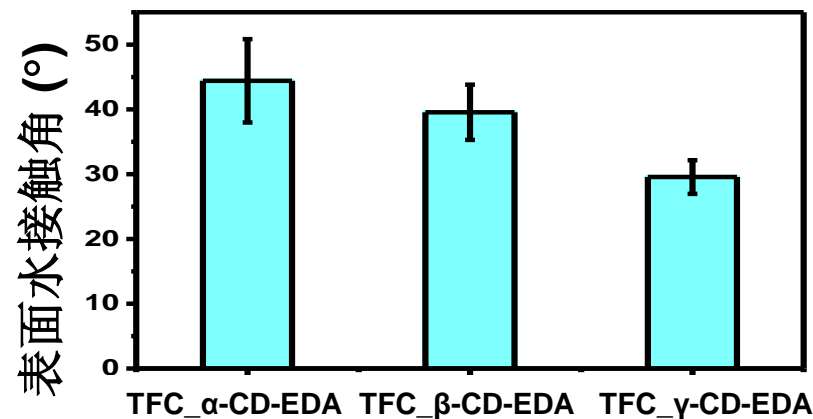
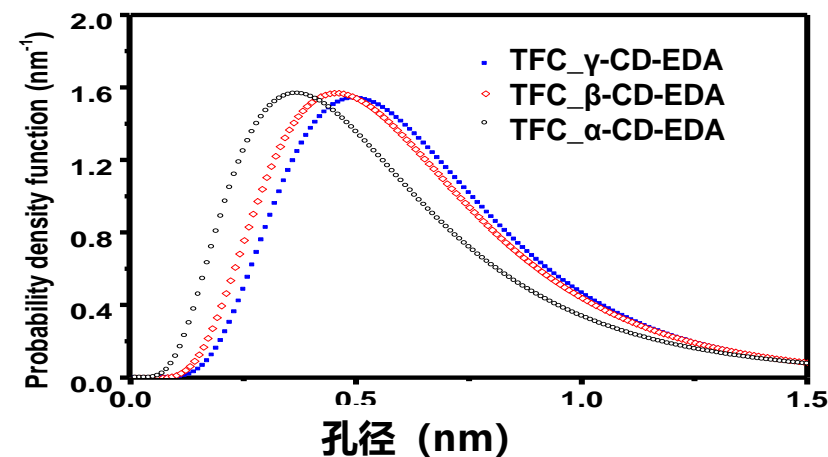


疏水性孔:

$\text{TFC}_\alpha\text{-CD-EDA} < \text{TFC}_\beta\text{-CD-EDA} < \text{TFC}_\gamma\text{-CD-EDA}$

亲水性孔:

$\text{TFC}_\alpha\text{-CD-EDA} > \text{TFC}_\beta\text{-CD-EDA} > \text{TFC}_\gamma\text{-CD-EDA}$

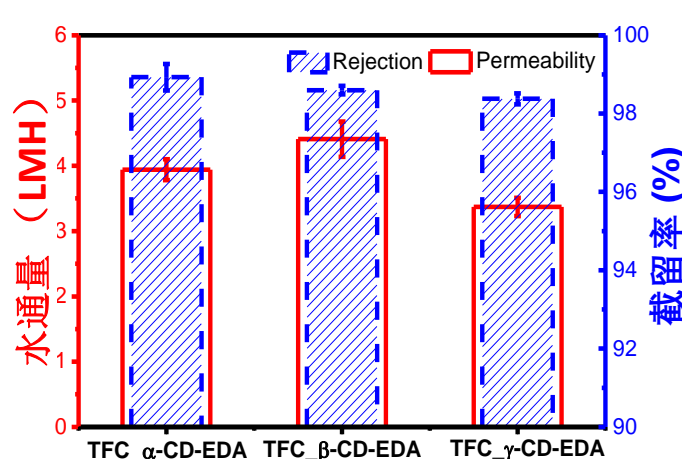


PA层微孔结构调控

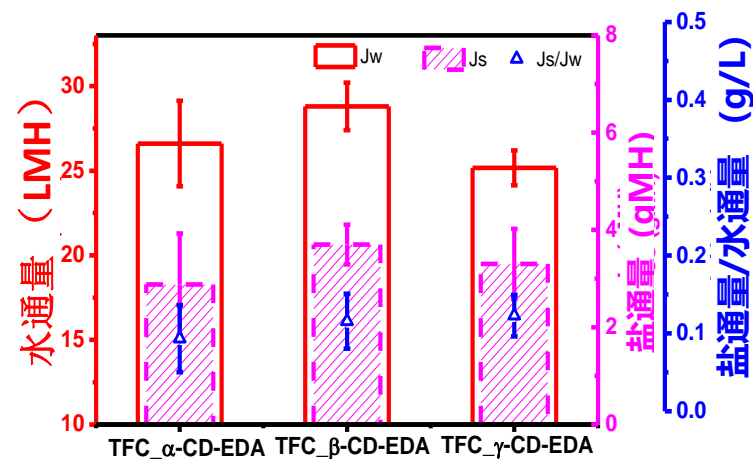
乙二胺功能化环糊精(CD-EDAs)对PA层的改性 膜分离性能

亲水性孔:

TFC_α-CD-EDA
> TFC_β-CD-EDA
> TFC_γ-CD-EDA
疏水性孔:
TFC_α-CD-EDA
< TFC_β-CD-EDA
< TFC_γ-CD-EDA



*2 bar, 1000 ppm Na₂SO₄溶液

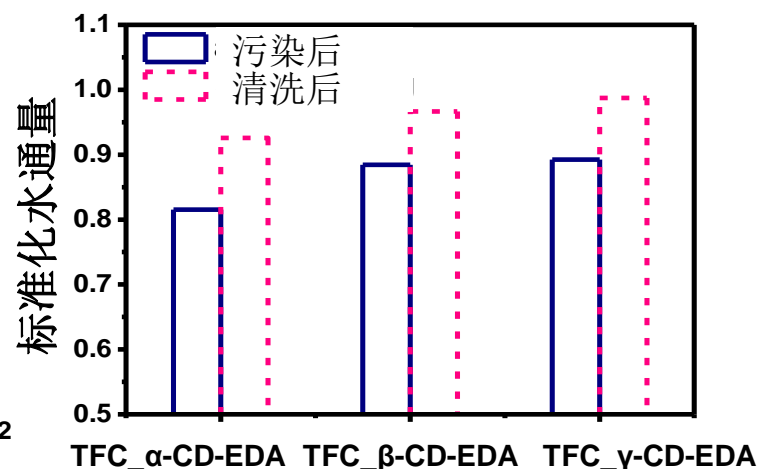
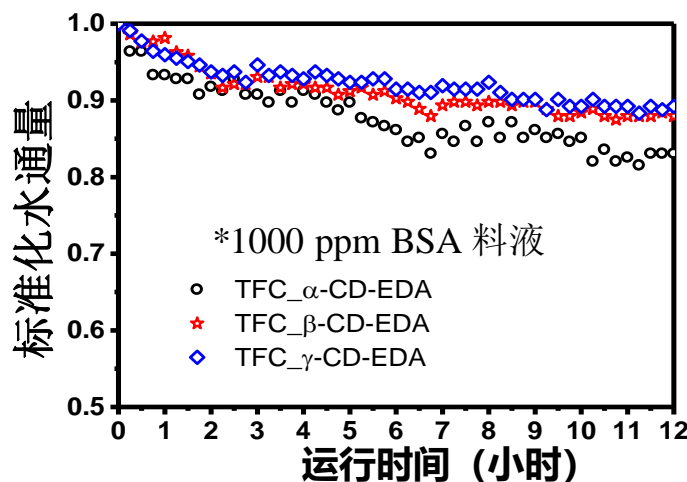


* FO 模式, 料液: 去离子水; 汲取液: 0.5 M Na₂SO₄ 溶液

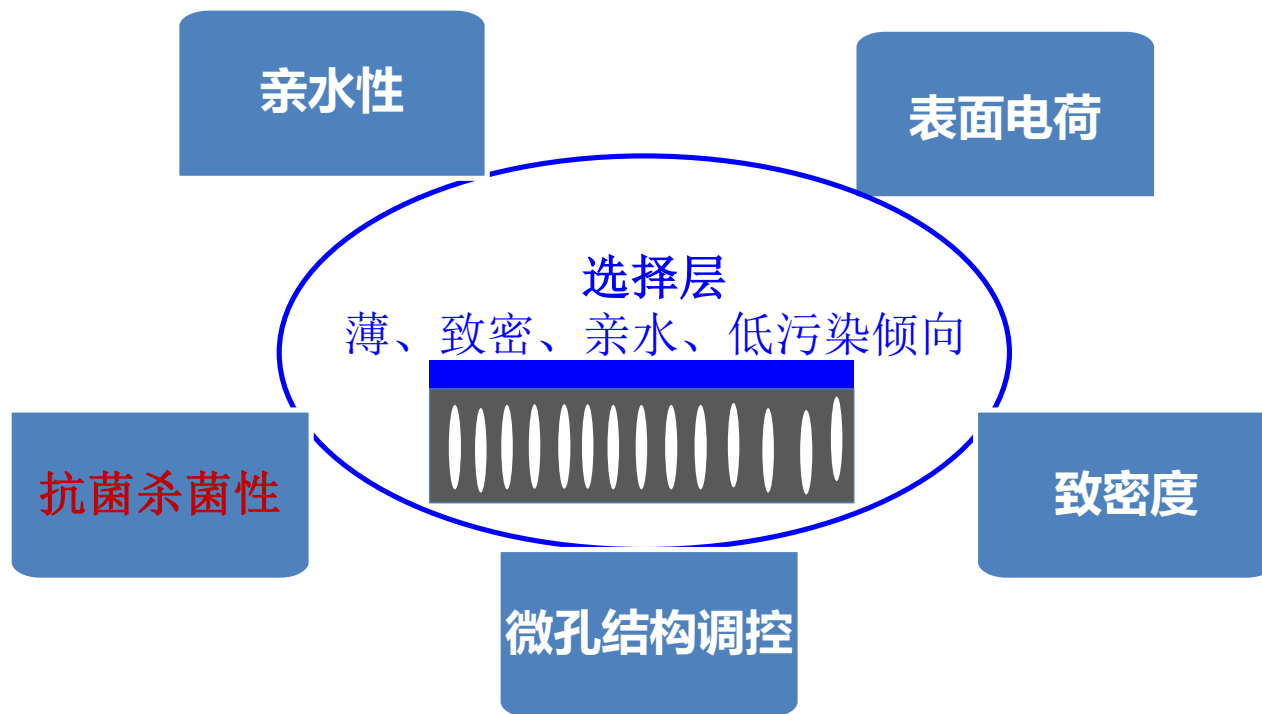
抗污染性能

亲水性:

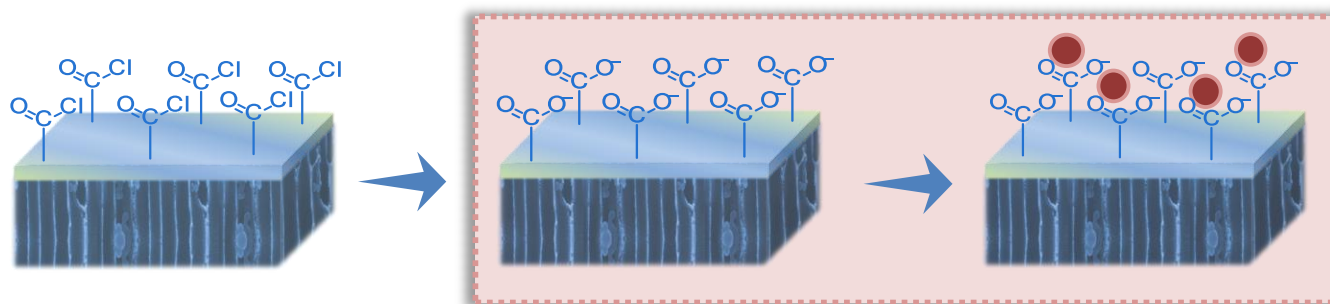
TFC_α-CD-EDA
< TFC_β-CD-EDA
< TFC_γ-CD-EDA
粗糙度:
TFC_α-CD-EDA
< TFC_β-CD-EDA
< TFC_γ-CD-EDA



报告内容



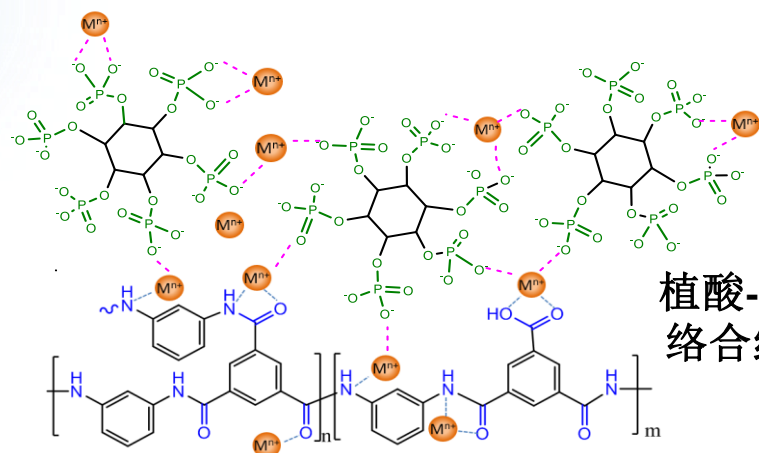
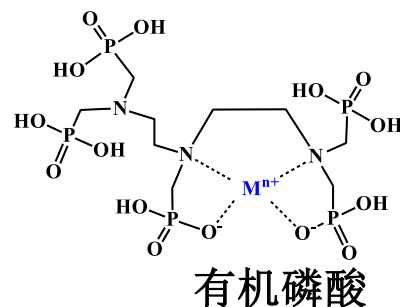
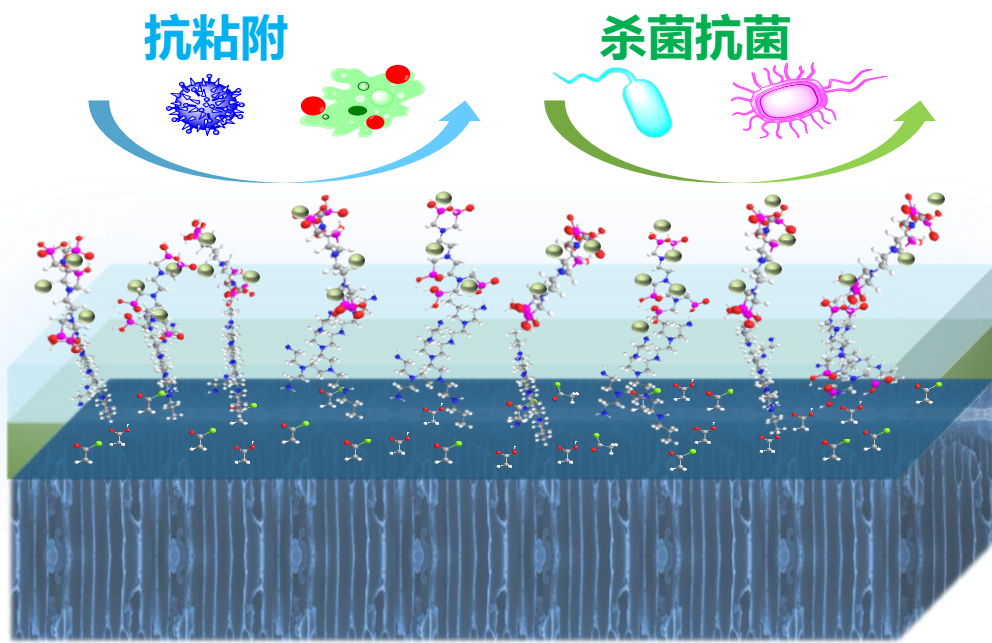
膜表面抗菌改性



抗菌剂的直接接枝改性:

× 反应活性低

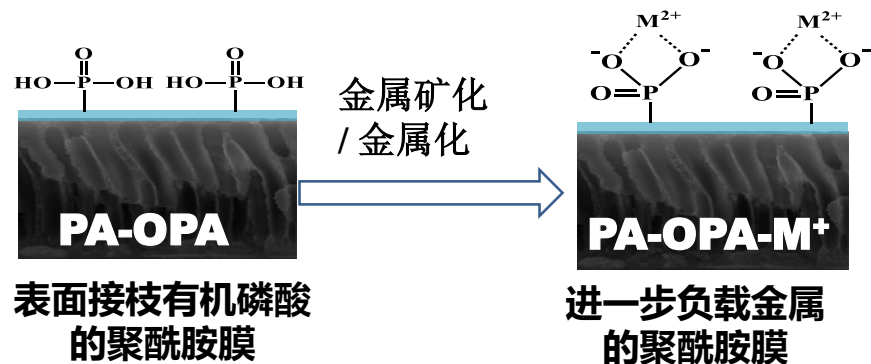
× 反应位阻大



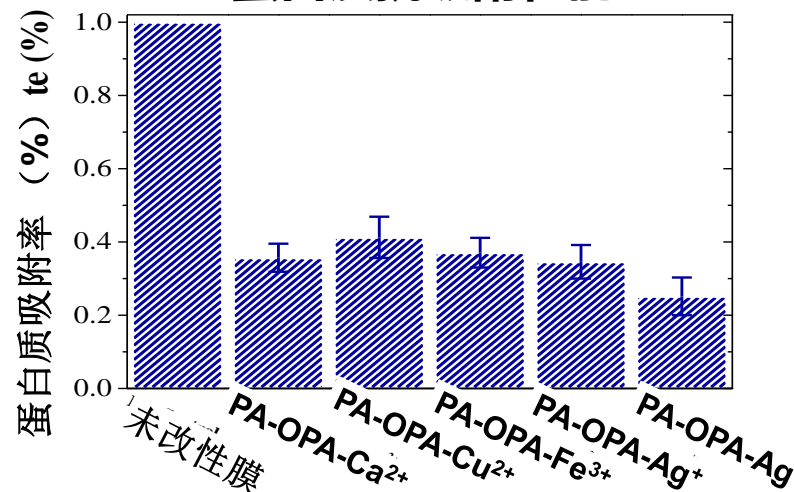
- L. Shen, et al, JMS, 2019, 586, 84–97.
- Yi M. et al., ACS Appl. Mater. Interfaces 2019, 11, 15698.
- Xiong S. et al, Environ. Sci. Technol. 2019, 53, 3331–3341.

膜表面抗菌改性

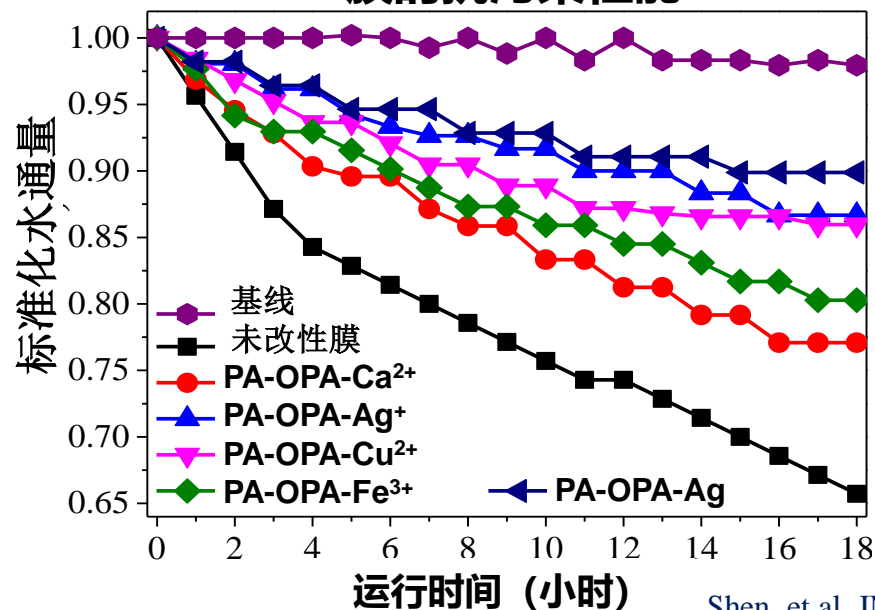
有机磷酸对膜表面的离子化和矿化处理



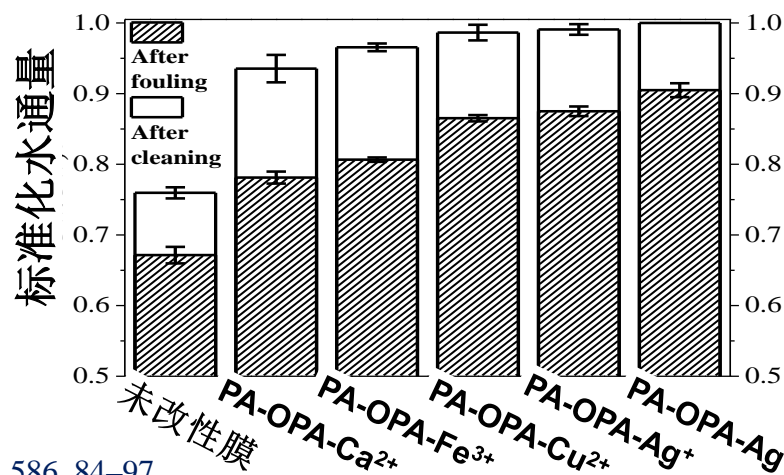
蛋白质抗吸附性能



膜的抗污染性能



膜的通量恢复率



膜表面抗菌改性

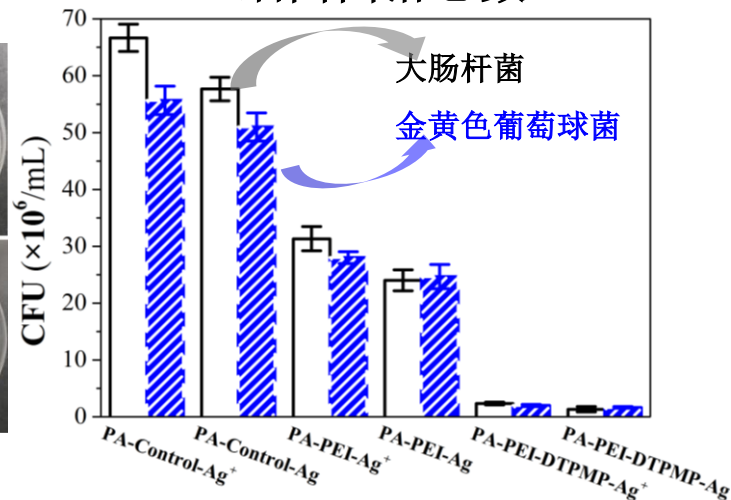
有机磷酸对膜表面的离子化和矿化处理

抗菌性能

大肠杆菌

金黄色葡萄球菌

细菌菌落总数



PA-Control-Ag⁺

PA-Control-Ag

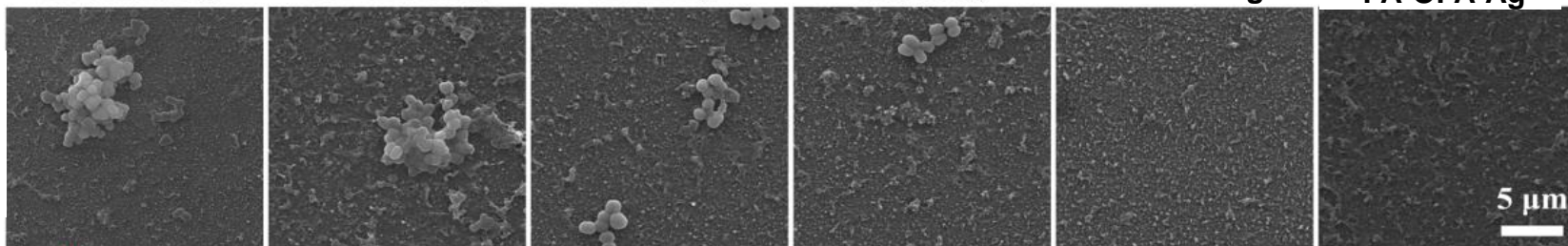
PA-PEI-Ag⁺

PA-PEI-Ag

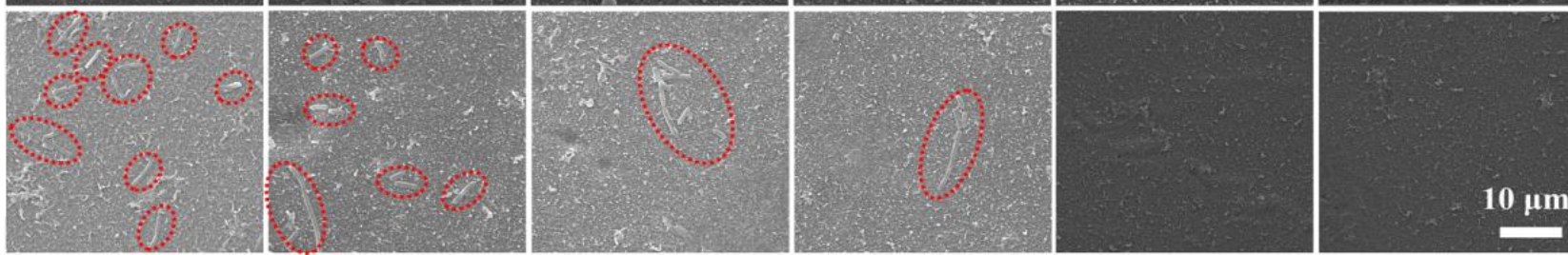
PA-OPA-Ag⁺

PA-OPA-Ag

金黄色葡萄球菌



大肠杆菌



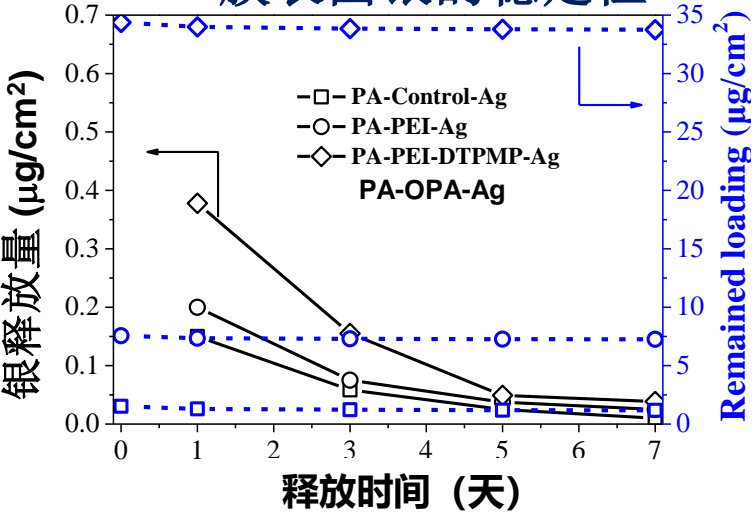
膜表面抗菌改性

有机磷酸对膜表面的离子化和矿化处理

银负载量

PA-Control-Ag	PA-PEI-Ag					PA-OPA-Ag
膜	C	O	N	P	Ag	
直接接Ag离子膜	72.11	16.47	11.28	0	0.14	
直接接Ag膜	70.8	17.73	10.94	0	0.53	
PA-PEI接Ag离子膜	71.39	13.88	14.41	0	0.32	
PA-PEI接Ag膜	70.21	14.31	14.7	0	0.78	
PA-OPA接Ag离子膜	70.65	15.52	13.05	0.27	0.51	
PA-OPA接Ag膜	67.89	16.23	13.53	0.56	1.79	

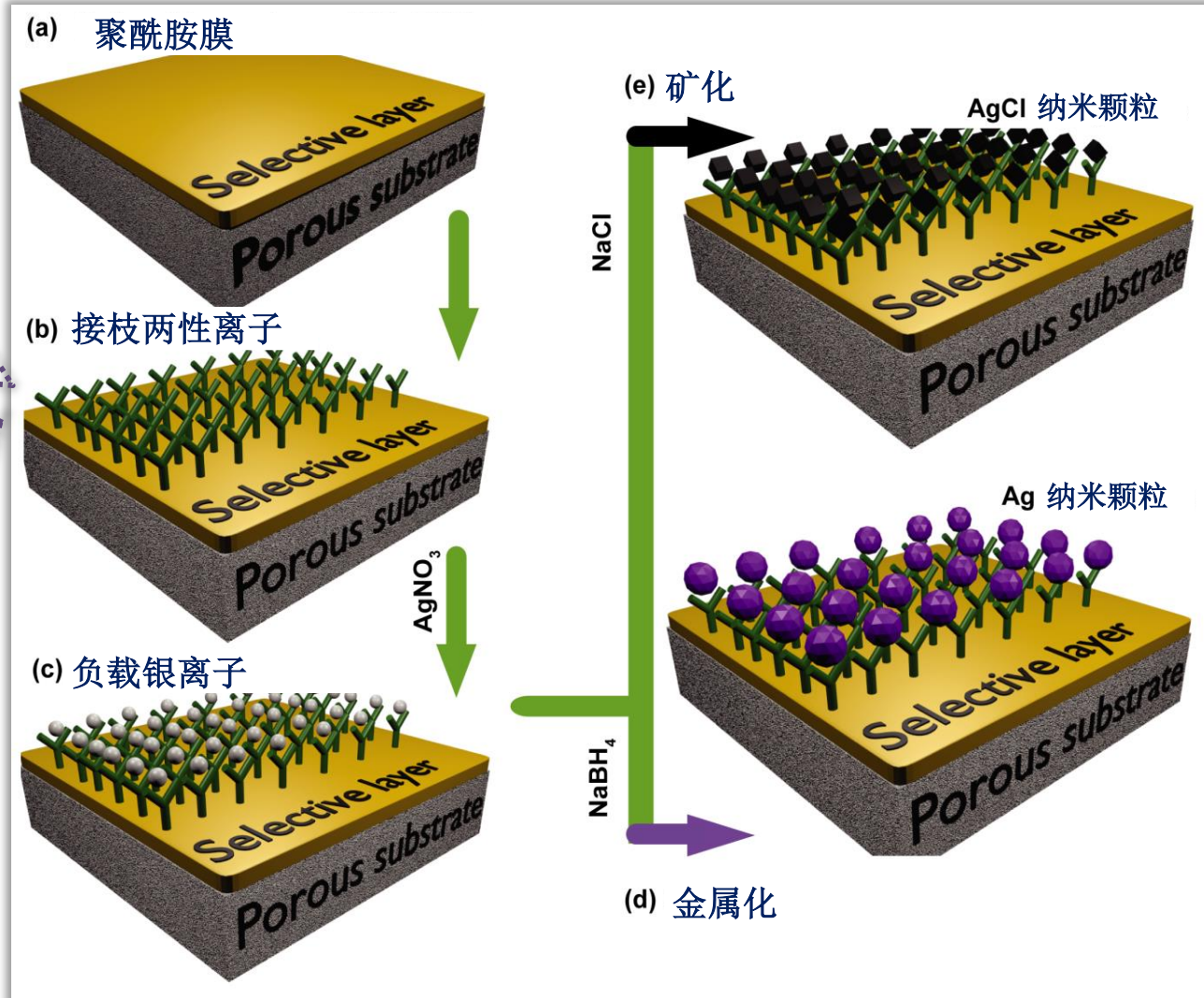
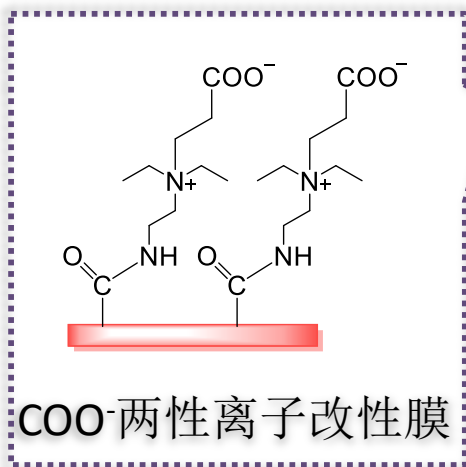
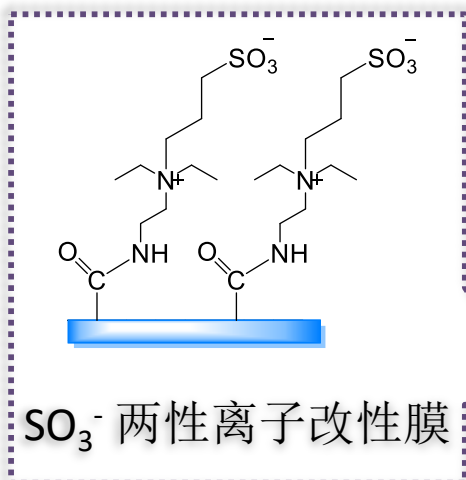
膜表面银的稳定性



膜	接种方法	改性化合物	稳定释放量 ($\mu\text{g}/\text{cm}^2$)	总载量 ($\mu\text{g}/\text{cm}^2$)	有效时间 (day)
PA-OPA-Ag	间接	PEI/DTPMP	0.04	34.38	850
TFC-S-Ag	间接	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{SH}$	0.1	15.5	155
TFC-APD-Ag	直接	电弧等离子体沉积	0.011	1.075	97
TFC-Ag@SiO ₂	间接	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{SH}$	0.0011	0.155	140
TFC-Ag	直接	/	0.01-0.1	0.8-3.7	127
TFC-S-Bio-Ag	间接	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{SH}$	0.02	0.38	340
TFC-S-Chem-Ag	间接	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{SH}$	0.02	2.28	190

膜表面抗菌改性

两性离子-银络合物的表面改性



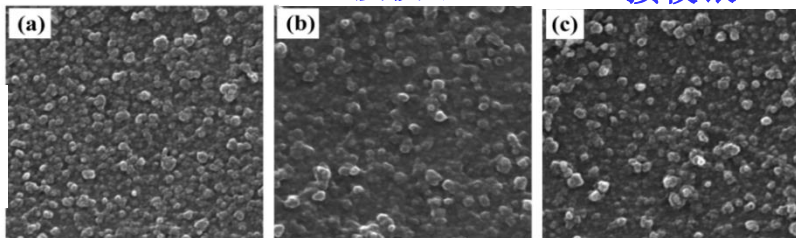
- ✓ 相同的电荷单位
- ✓ 优越的亲水性
- ✓ 更致密更厚的水合层

膜表面抗菌改性

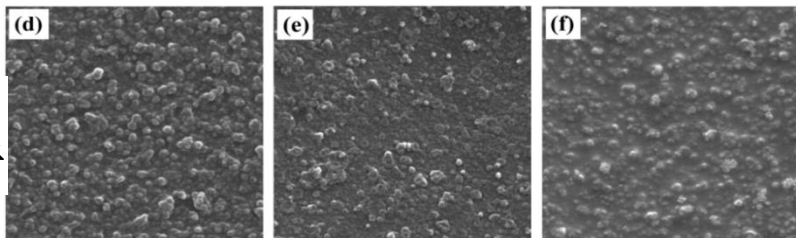
两性离子-银络合物的表面改性

直接银接枝 SO_3^- -两性离子接枝银 COO^- -两性离子接枝银

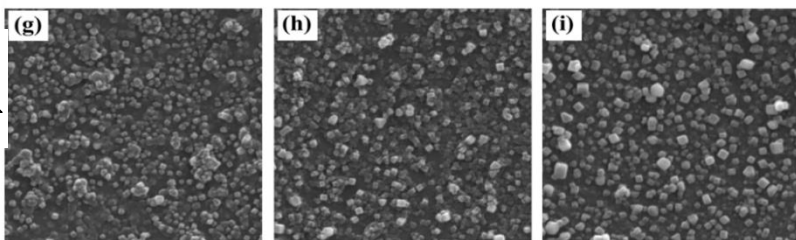
未接枝银



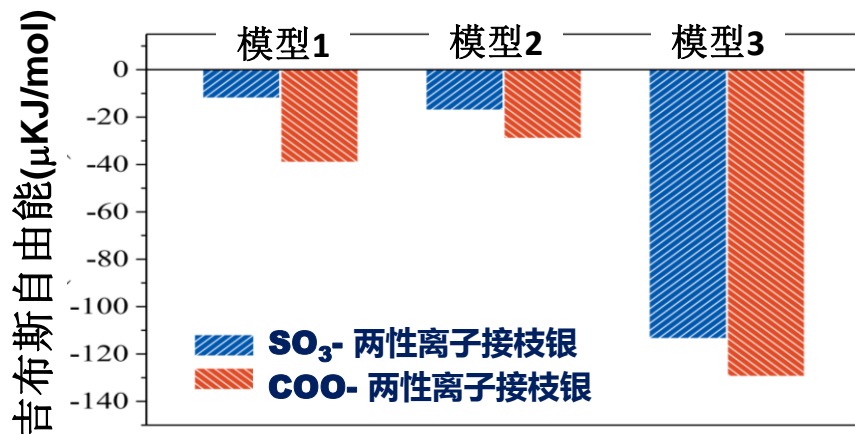
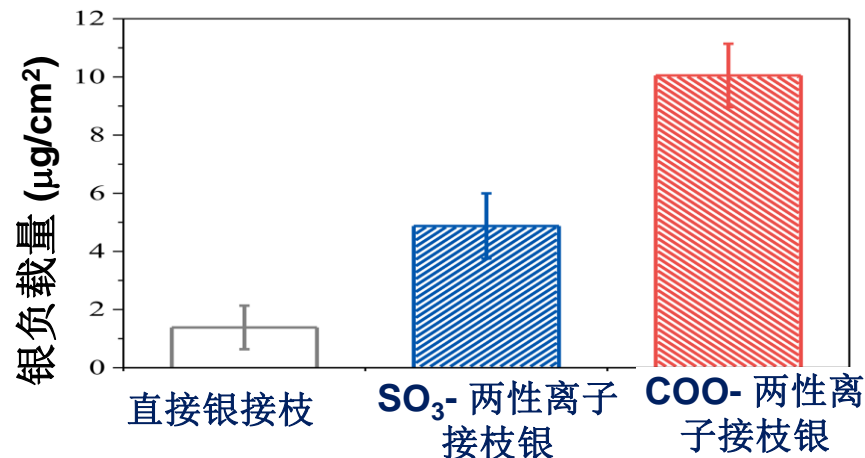
接枝银原子



接枝银离子



Scale bar: — 1 μm



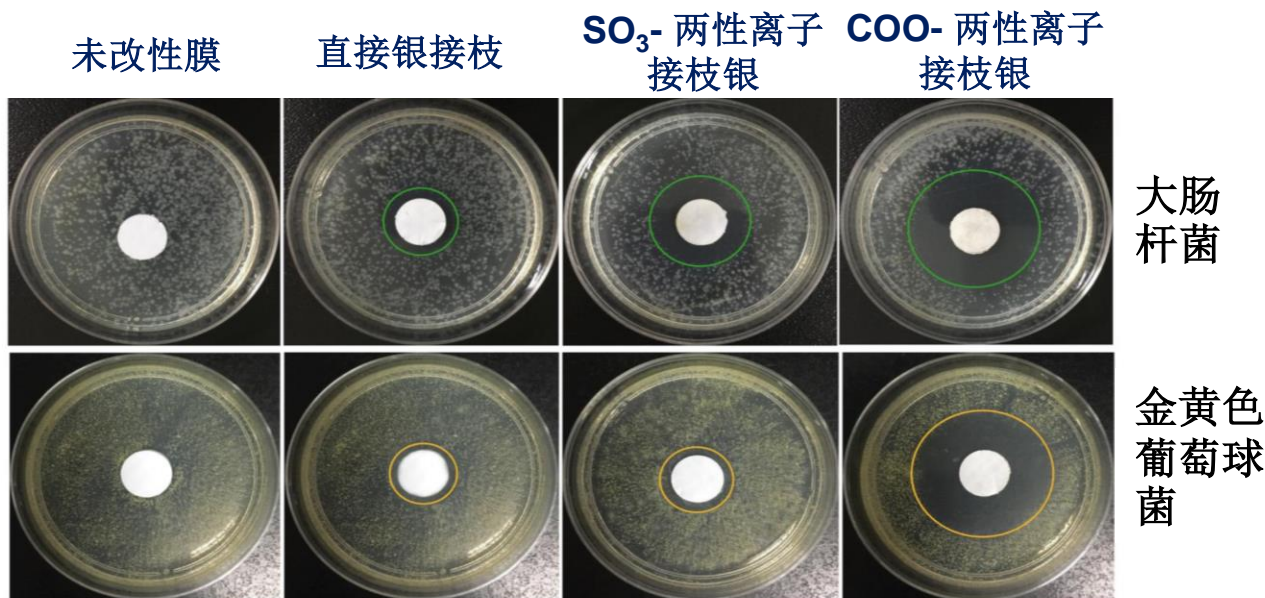
为何 COO^- -两性离子接枝银改性膜优于 SO_3^- -两性离子接枝银改性膜?

➤ COO^- -Ag络合物在热力学上更易形成，使银纳米粒子更易在 COO^- -两性离子-Ag膜表面成核。

膜表面抗菌改性

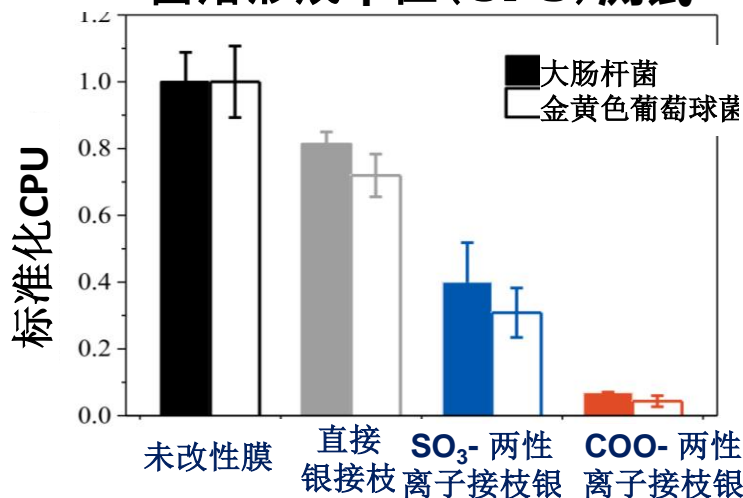
两性离子-银络合物的表面改性

抑菌圈测试

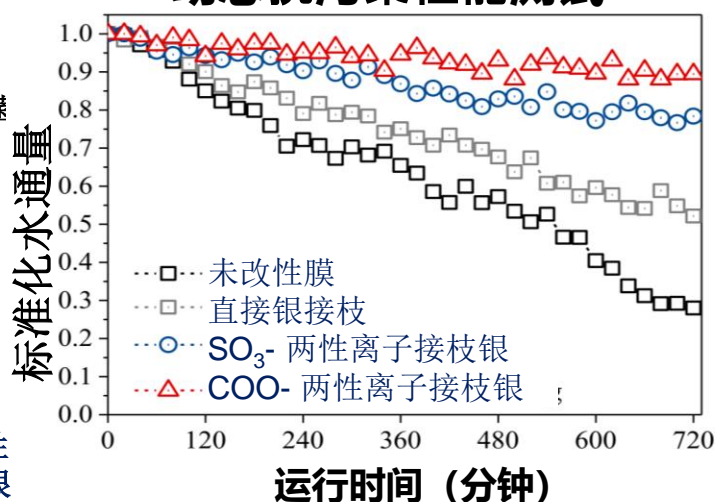


✓ 两性离子预接枝可有效提升银负载量, 进一步提高膜的抗菌性能

菌落形成单位(CFU)测试

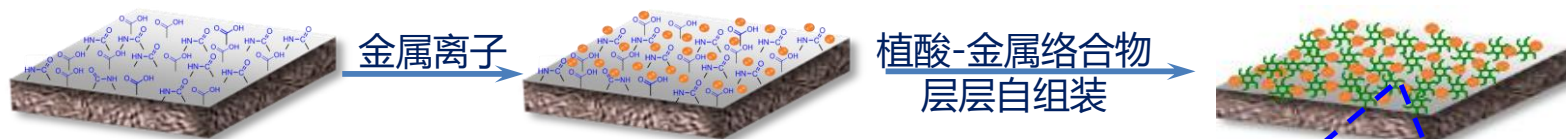


动态抗污染性能测试



膜表面抗菌改性

植酸-金属在膜表面的层层自组装

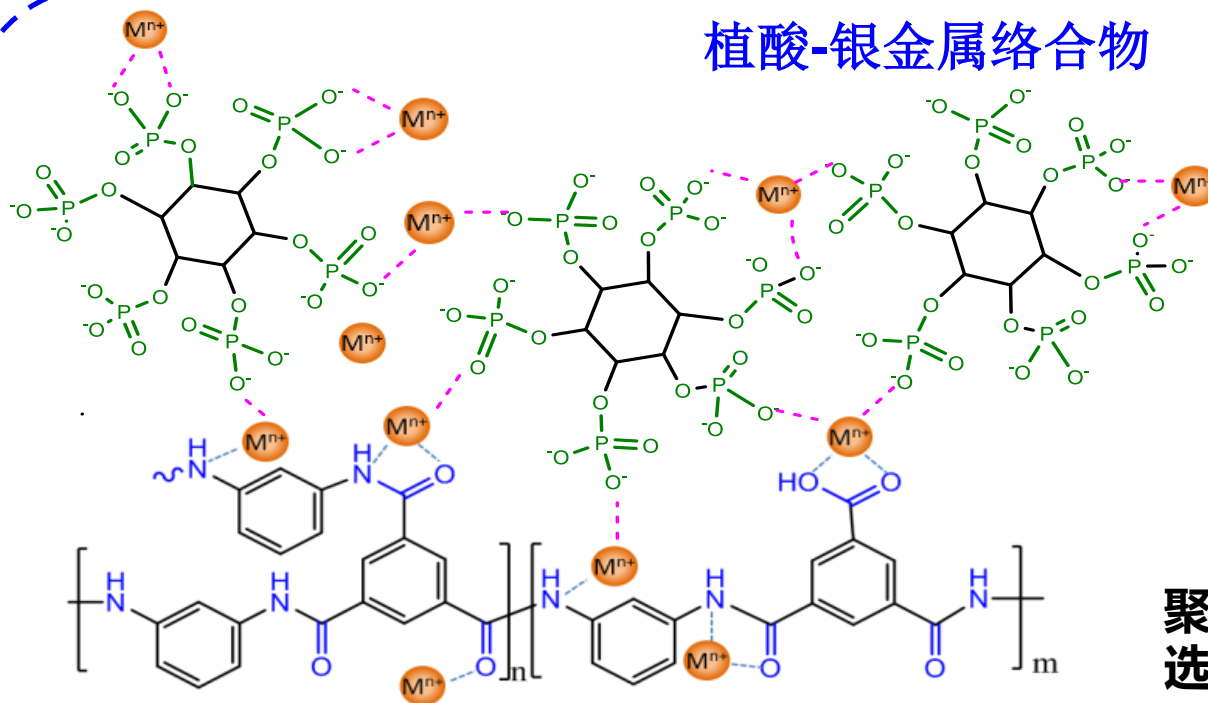


● M^{n+} Ag/Cu离子

植酸

Xiong S. et al,
Environ. Sci. Technol.
2019, 53, 3331–3341.

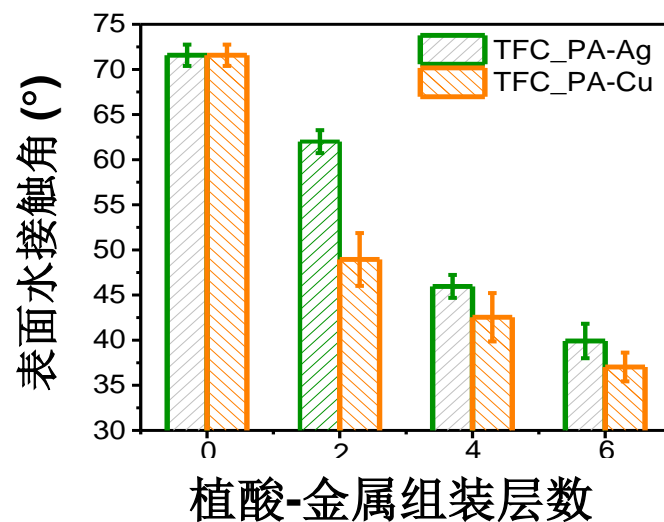
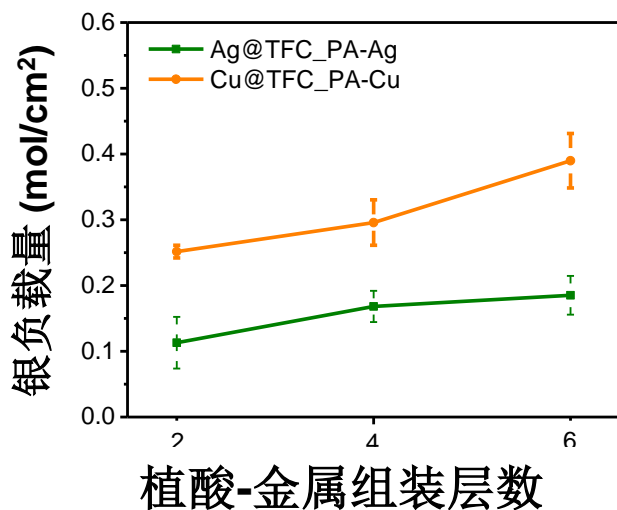
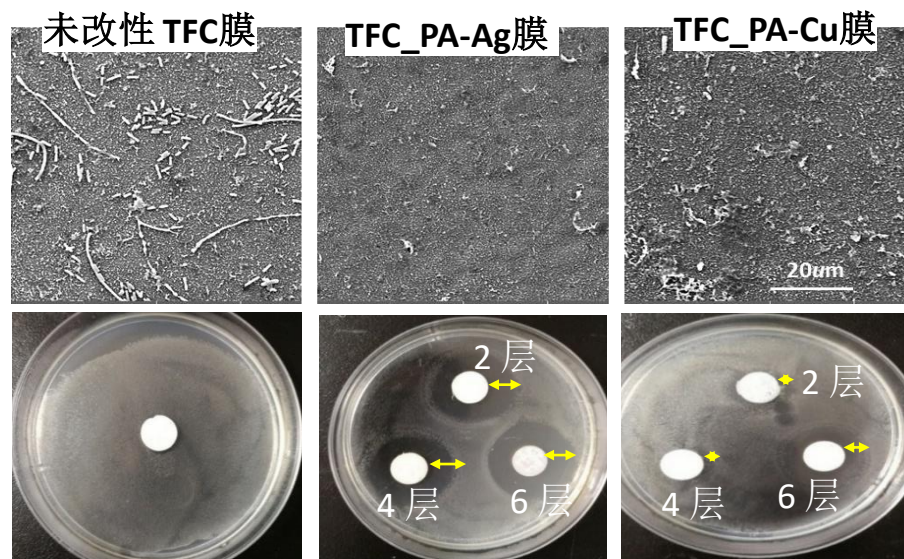
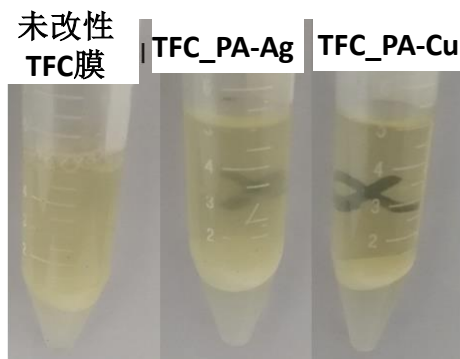
植酸-银金属络合物



膜表面抗菌改性

植酸-金属在膜表面的层层自组装

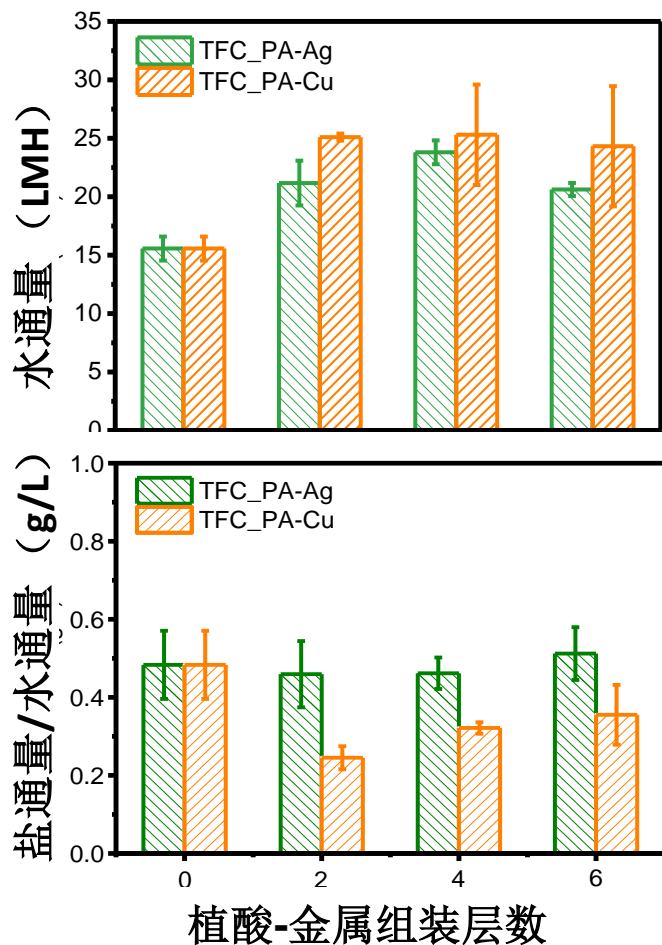
静态
污染
测试



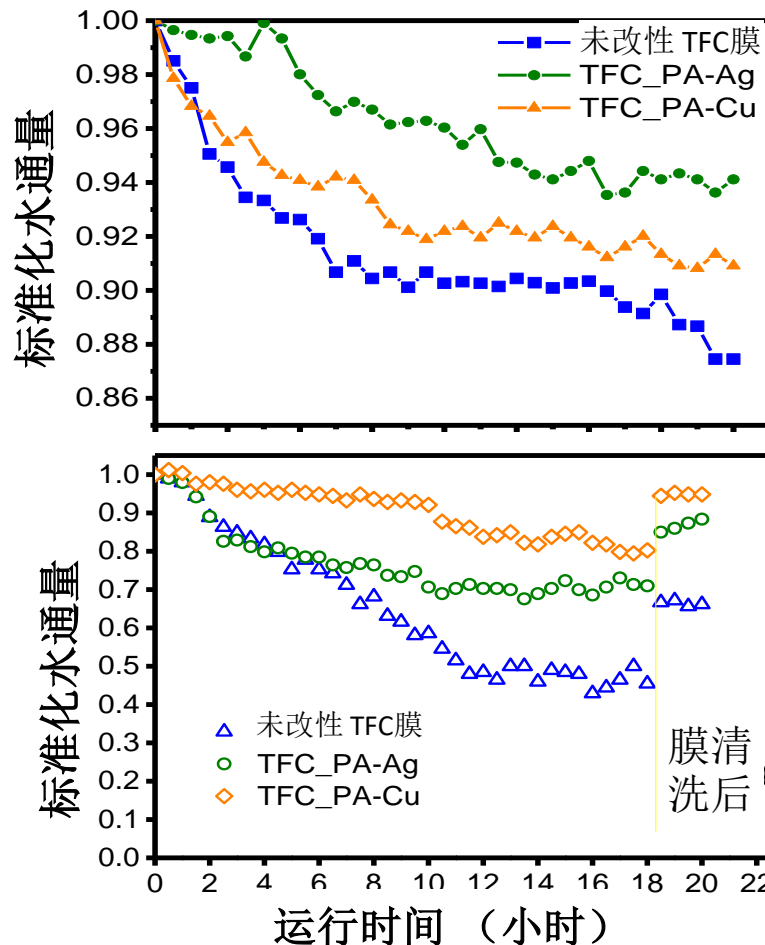
膜表面抗菌改性

植酸-金属在膜表面的层层自组装

膜的分离性能



动态抗污染性能



结 论

选择层

薄、致密、亲水、低污染倾向

亲水性

- 含胺基硅氧烷
- 多胺单体
- 氧化石墨烯

表面电荷

- 接枝有机磷酸

致密度

- 叔胺催化剂
- 超声辅助

微孔结构调控

- 超声辅助
- 胺改性的环糊精单体

抗菌性

- 银接枝
- 间接接枝

支撑层

疏松、亲水、较低的孔曲率、机械稳定性

亲水性

- 表面碱处理
- 亲水性PFSA掺杂

孔隙率

- PFSA掺杂
- SiO₂@MWCNT掺杂

对选择层影响

- 磷酸改性TiO₂



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谢谢大家！

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