

Electronic Supplementary Information (ESI):

Polyacrylonitrile Nanofiber Membranes Modified with Ionically Crosslinked Polyelectrolyte Multilayers for the Separation of Ionic Impurities

Sahadevan Rajesh¹, Yong Zhao², Hao Fong² and Todd J. Menkhaus^{1}*

¹Department of Chemical and Biological Engineering

²Department of Chemistry and Applied Biological Sciences

South Dakota School of Mines and Technology

Rapid City, SD 57701

**Corresponding author:*

Todd J. Menkhaus, Ph.D.

Professor

Department of Chemical and Biological Engineering

South Dakota School of Mines and Technology

501 East Saint Joseph Street

Rapid City, SD 57701

Email: Todd.Menkhaus@sdsmt.edu

Phone: (605) 394-2422

Fax: (605) 394-1232

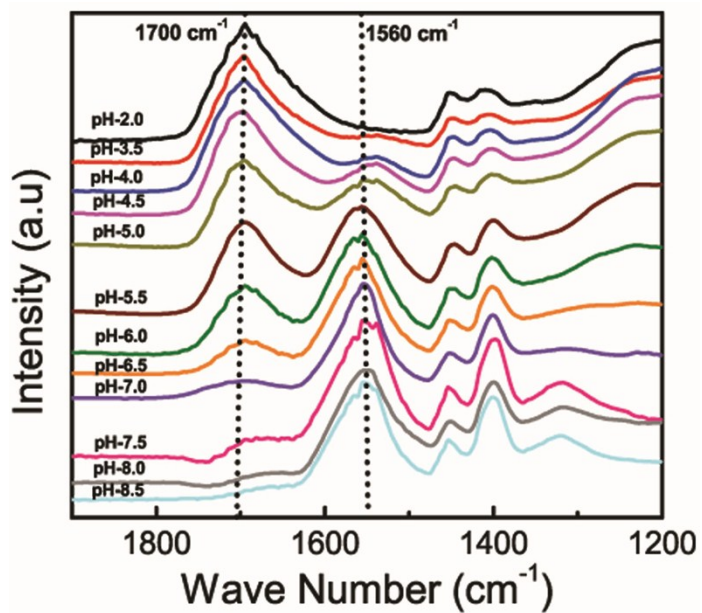
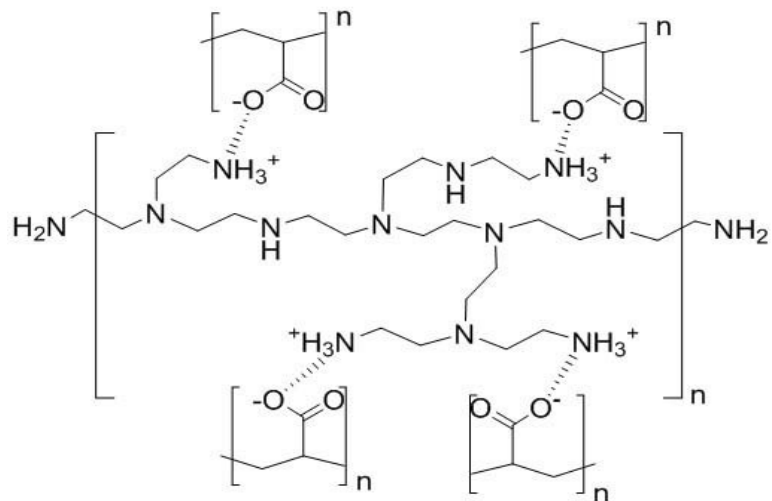


Fig. S1. ATR-FTIR spectra of the PAA films casted from aqueous solutions at various pHs used to calculate the degree of ionization of PAA. 20 mM PAA solution prepared in deionized water without salt casted on to a silicon wafer substrate was used for the ATR-FTIR measurements (the degree of ionization of PAA calculated from this ATR-FTIR spectra are given in Figure 1b, and compared to ATR-FTIR spectra in the presence of 0.5 M NaCl in Figure 1a).



Scheme S1. Possible ionic cross linking mechanism between the protonated amine group of BPEI (pH-10.0) and deprotonated carboxylate group of PAA (pH-3.5) in the multilayer assembly of BPEI/PAA.

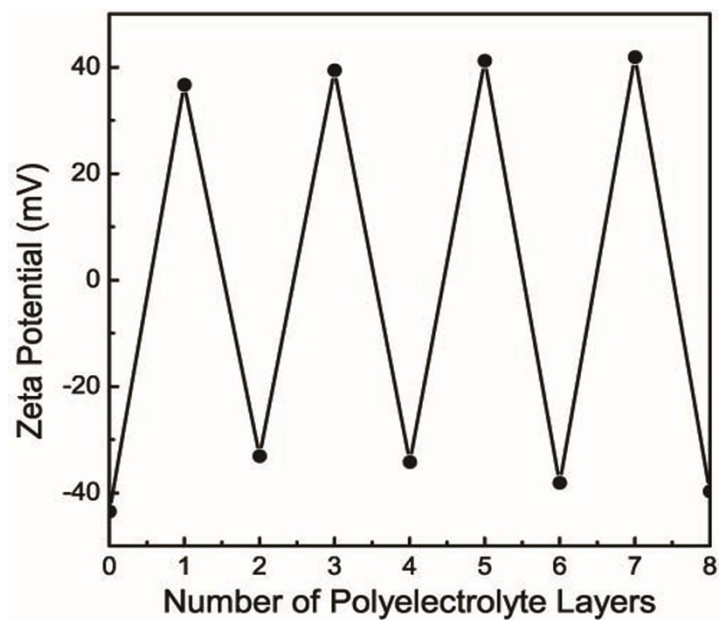


Fig. S2. Alternation in zeta potential with layer number for BPEI/PAA multilayer coated on silica nano particles. 0.2 wt.% of BPEI (pH-10.0) and 0.4 wt.% of PAA (pH-3.5) prepared in DI water was used for the LbL deposition. 0.5M NaCl was used as the supporting electrolyte. Zeta potential of the bare silica nano particles dispersed in DI water was -43.5 mV.

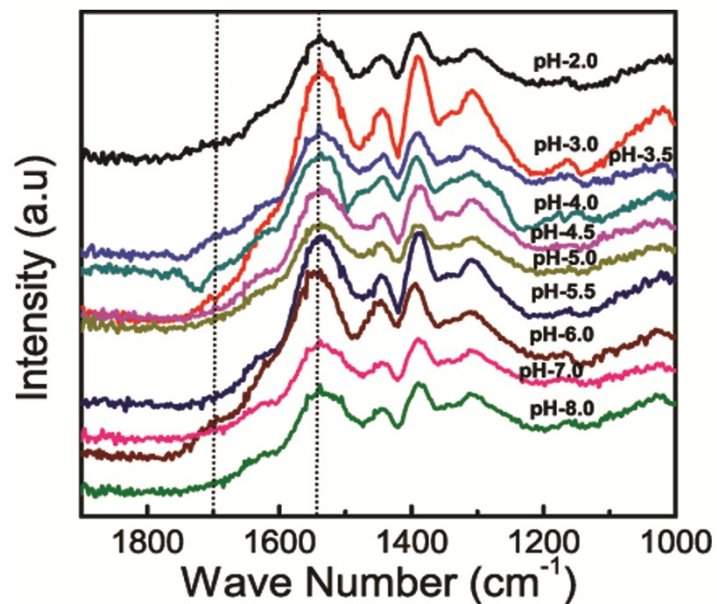


Fig. S3. ATR-FTIR spectra of BPEI/PAA films at various post assembly pH treatment. BPEI/PAA multilayer deposited on to a silicon wafer substrate was immersed in desired pH for 10 minutes and used for the ATR-FTIR measurements. Degree of ionization of PAA at given pH was estimated based on adsorption bands of carboxylic group (COOH) at 1700cm⁻¹ and carboxylate anion at 1550cm⁻¹.

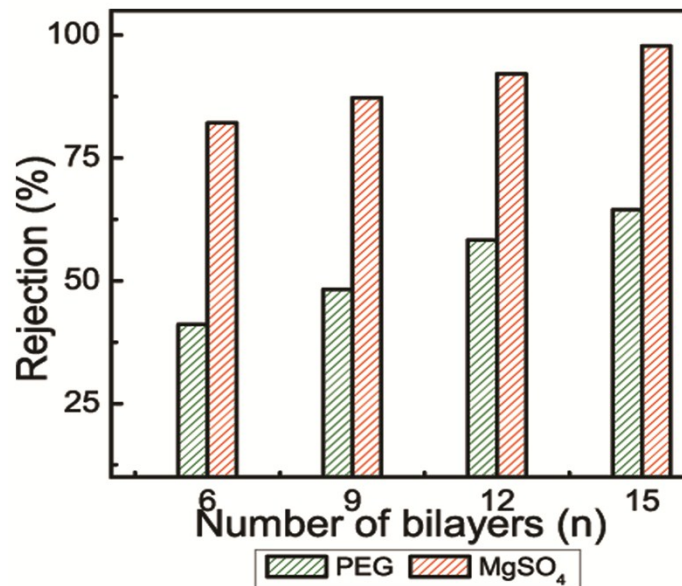


Fig. S4. Rejection results of PAN nanofiber composite membranes modified by Layer-by-Layer assembly. Rejection results of the PEG molecules (PEG-3.5 kDa) and Mg²⁺ in a mixture of PEG and MgSO₄. 500 ppm solution of PEG-3.5 kDa mixed with 1000 ppm solution of MgSO₄ was used as the feed solution. Concentration of PEG in the feed and permeate was estimated using Total Organic Carbon Analyser (TOC). Mg²⁺ concentration in this mixture was estimated using Inductively Coupled Plasma Spectroscopy (ICP).

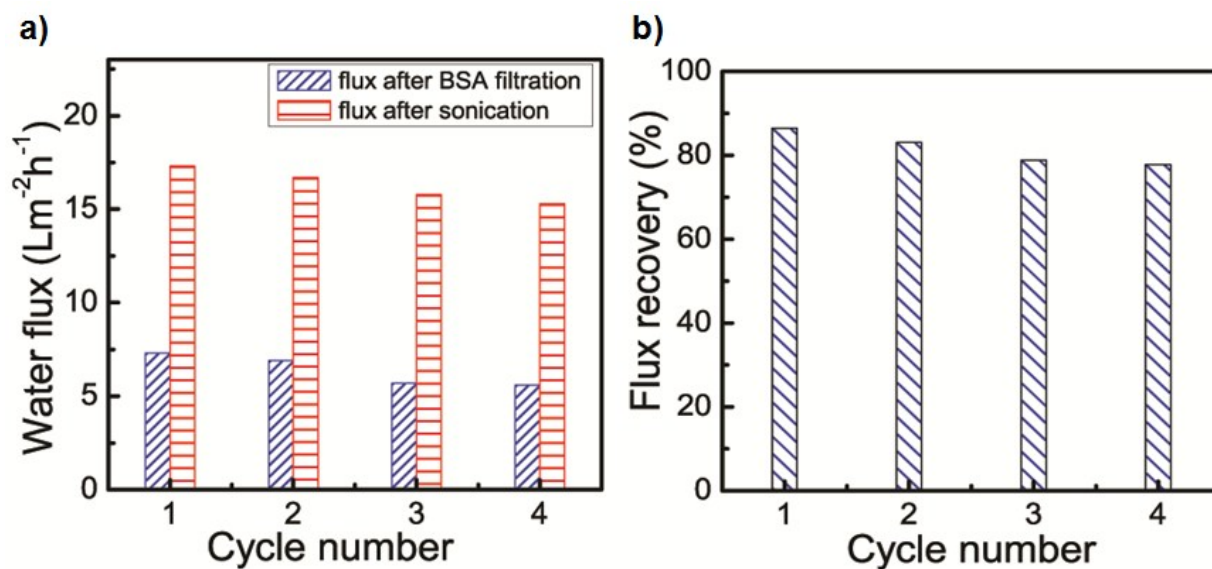


Fig.S5. Filtration stability (fouling and cleaning for multiple operating cycles) of the PAN nanofiber membranes modified with 15 bilayers of BPEI/PAA. (a) pure water flux of the membrane after filtration with a BSA solution, and following the subsequent sonication assisted washing, (b) percentage flux recovery of the PAN nanofiber membranes, which is the ratio of water flux after sonication to the initial water flux. These membranes have shown an initial pure water flux of $20.1 \text{ Lm}^{-2}\text{h}^{-1}$. Filtration experiments were carried at an applied pressure of 4 bar for six hours, using bovine serum albumin (BSA) with an initial concentration of 100 mg L^{-1} and concentration factor of approximately 3x during the process.

Table S1: Comparative evaluation of the performance of the BPEI/PAA modified PAN nanofibrous membranes with recently reported NF membranes in the literature

S. No	Brief description of the membrane modification involved	Pure Water Flux (L m ⁻² h ⁻¹)	Rejection (%) & Solute tested	Applied Pressure (in bar)
1, This work	Ionic crosslinked BPEI/PAA multilayers modified PAN Nanofibrous membranes	19.4	98.7, MgSO ₄	4
2	NF 90, Dow Filmtec	10.4	99.6, MgSO ₄	4
3	Polyacrylonitrile (PAN) asymmetric membranes modified with poly(ethyleneimine) modified GO sheets and PAA by LbL ¹	8.4	99.5, congo red	10
4	Microporous PES asymmetric membrane modified by LbL with poly(ethyleneimine) and trimesoyl chloride ²	24.5	94.4%, MgSO ₄	8
5	Poly (amide-co-ester) TFC type membrane on polyethylene support using trimesoyl chloride (TMC) and glucose as monomers ³	42.5	93.8, glucose	10
6	O-(carboxymethyl)-chitosan surface functionalized with Graphene sheets ⁴	26.9	93.8, Na ₂ SO ₄	15
7	Novel positively charged copolymer membranes from poly (ether ether ketone) (PEEK) bearing pendant tertiary amine groups ⁵	12.6	99.4, MgCl ₂	4
8	Polyacrylonitrile (PAN) membranes surface modified with GO sheets and varies polycations by LbL ⁶	6.4/bar	99.2, methylene blue	5
9	TFC type NF membranes from TMC and m-phenylenediamine and subsequent modification with ethylenediamine ⁷	31.0	76.0, MgSO ₄	10
10	NF membranes prepared by assembly graphene and multiwalled carbon nanotubes ⁸	11.3/bar	83.5, Na ₂ SO ₄	5
11	Modification with GO nanosheets with amine enrichment ⁹	5.0/bar	96.3, MgCl ₂	1
12	PAN TFC membranes prepared by dip coating and insitu cross linking with quaternized PEEK with some tertiary amine groups ¹⁰	11.8	99.4, MgCl ₂	4
13	High performance TFC membrane prepared by incorporating porous filler ZIF-8 ¹¹	27.1	99.8, congo red	10
14	Multilayered TFC type membranes prepared on cellulose nanofibrous by a specific designed instrument for organic	94.3	96.7, MgSO ₄	4.8

	solution delivery ¹²			
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Supporting References

1. N. Wang, S. Ji, G. Zhang, J. Li and L. Wang, *Chem Eng J*, 2012, **213**, 318-329.
2. D. Wu, Y. Huang, S. Yu, D. Lawless and X. Feng, *J Membrane Sci*, 2014, **472**, 141-153.
3. W. Li, C. Bian, C. Fu, A. Zhou, C. Shi and J. Zhang, *J Membrane Sci*, 2016, **504**, 185-195.
4. J. Wang, X. Gao, J. Wang, Y. Wei, Z. Li and C. Gao, *Acs Appl Mater Inter*, 2015, **7**, 4381-4389.
5. X. Dong, S. Li, Q. Zhang and S. Zhang, *RSC Advances*, 2014, **4**, 22625-22631.
6. L. Wang, N. Wang, J. Li, J. Li, W. Bian and S. Ji, *Sep Purif Technol*, 2016, **160**, 123-131.
7. J. Zhang, Y. Hai, Y. Zuo, Q. Jiang, C. Shi and W. Li, *J Mater Chem A*, 2015, **3**, 8816-8824.
8. Y. Han, Y. Jiang and C. Gao, *Acs Appl Mater Inter*, 2015, **7**, 8147-8155.
9. Y. Zhang, S. Zhang and T.-S. Chung, *Environ Sci Technol*, 2015, **49**, 10235-10242.
10. X. Dong, Q. Zhang, S. Zhang and S. Li, *J Colloid Interf Sci*, 2016, **463**, 332-341.
11. L. Wang, M. Fang, J. Liu, J. He, J. Li and J. Lei, *Acs Appl Mater Inter*, 2015, **7**, 24082-24093.
12. X. Wang, D. Fang, B. S. Hsiao and B. Chu, *J Membrane Sci*, 2014, **469**, 188-197.