Supplementary Information

Green synthesis of Nanoscale Anion Exchange Resin for Sustainable Water Purification.

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KEYWORDS

Water purification, NOM removal, adsorption, ion-exchange, SWCNT, poly(vbTMAC), kinetics, disinfection byproducts

LIST OF ABBREVIATIONS

ARGET	activators regenerated by electron transfer
ATRP	atom transfer radical polymerization
DBP	disinfection byproduct
DLS	dynamic light scattering
DMF	N,N-dimethylformamide
HAA	haloacetic acid
HEBiB	2-hydoxyethyl 2-bromoisobutyrate
HiPCO	high pressure carbon monoxide
mg-C/L	milligrams of carbon per liter of solution
MWCO	molecular weight cutoff
NaFL	sodium fluorescein
^{1}H NMR	nuclear magnetic resonance
NOM	natural organic matter
SEM	scanning electron microscopy
FE-SEM	Field emission-scanning electron microscopy
SWCNT	single-walled carbon nanotube
THM	trihalomethane
TOC	total organic carbon
TPMA	tris(2-pyridylmethyl)amine
USEPA	United States Environmental Protection Agency
vbTMAC	vinylbenzyl trimethylammonium chloride

Synthesis and Characterization of poly(vbTMAC) and **Aq-SNR**

Figure S1: After centrifugation at 100,000 RCF (1 h), the reaction mixture deposits at the walls of the polycarbonate tubes

Removal of brine from nanoresin:

Figure S2: Brine Removal from **Aq-SNR** dispersion. (A) **Aq-SNR** is the added in the form of dialyte and MilliQ is added as dialyzate. The dialyzate was replaced after every 2 h and the conductivity of dialyzate was checked as a function of the number of iterations. This confirms maximal removal of brine (<1 µS/cm)

ARGET-ATRP polymerization Scheme:
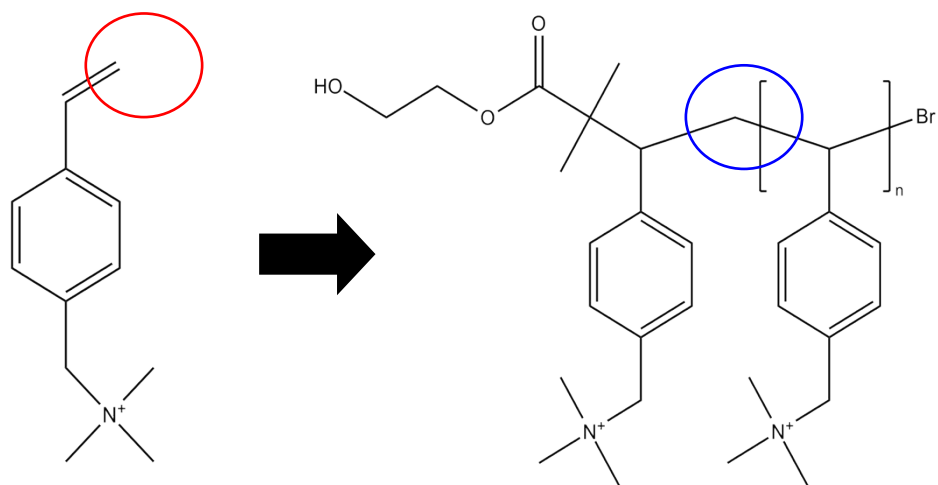
Figure S3: Reaction scheme showing the change from vinylic to allylic conditions for the terminal hydrogen.
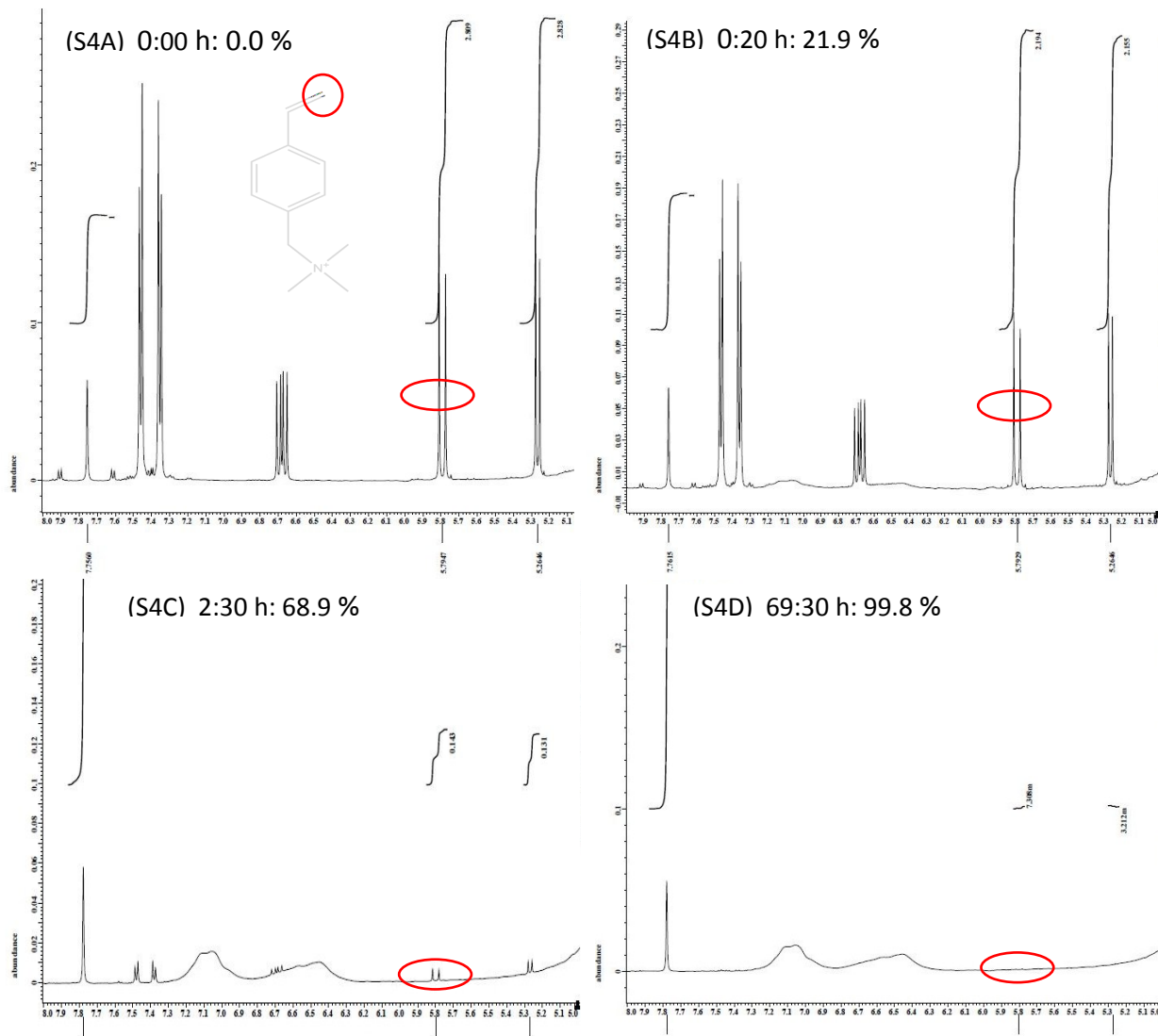
Percent Conversion of Monomer:

Figure S4A: ^{1}H NMR Spectra of reaction mixtures from polymerization reaction versus time. To monitor the conversion of vbTMAC monomer to polymer, the vinylic proton signal (5.8 ppm, 1H, d) decreases in relation to the DMF internal standard signal (7.8 ppm, 1H, s). The ratio between initial peak integration and the integration at time t is used to determine the percent conversion.
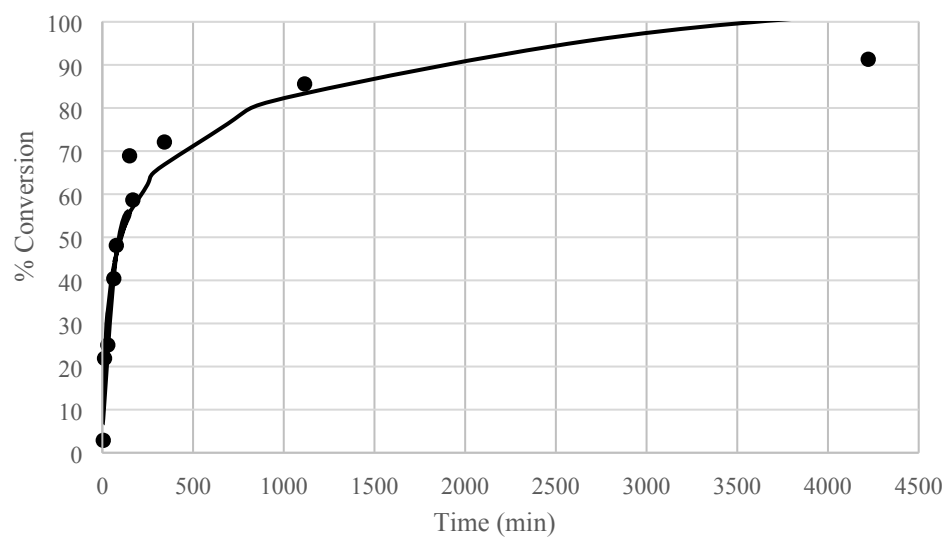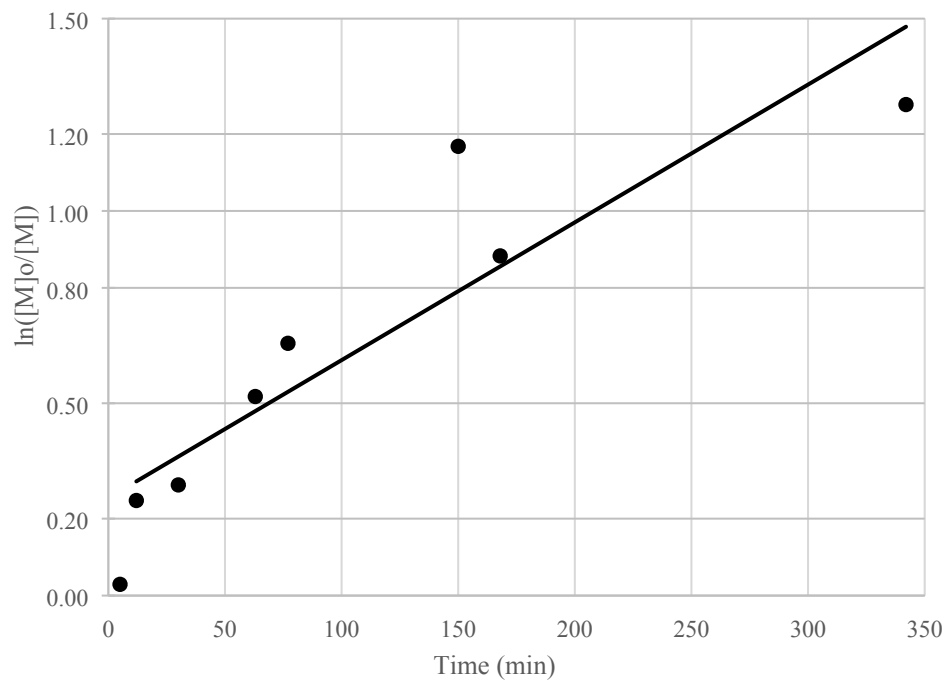
Figure S4B: Percent conversion (lower) and $ln([M]_o/[M])$ (upper) versus time. 40 min polymer growth results in 33% conversion of monomer.
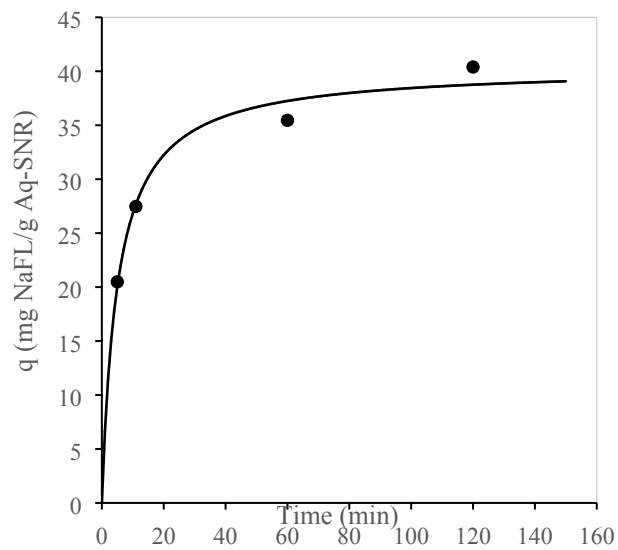
Figure S5: Adsorption kinetics of surrogate NOM NaFL into a thin **Aq-SNR** membrane. Pseudo-second order diffusive kinetics model fit to the data with a rate constant k = 0.0048 s^{-1} (mg/g)$^{-1}$
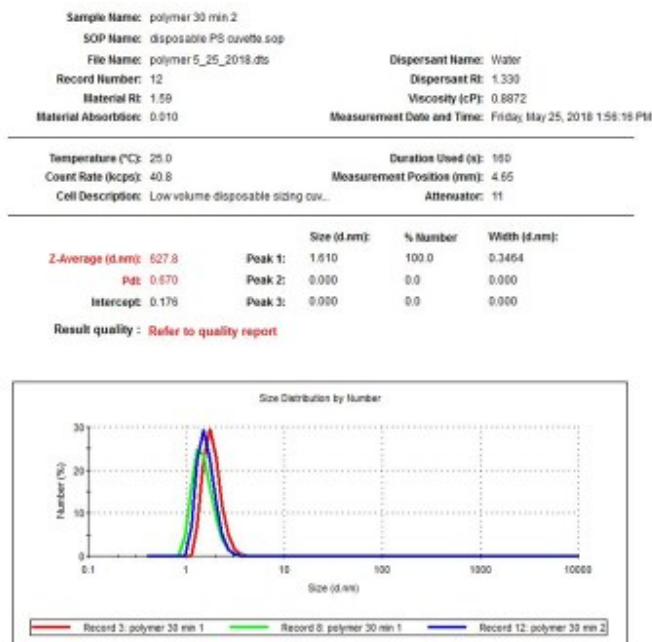
Figure : Number distribution of polymer grown for 30 minutes (sample is centrifuged, dialyzed and pushed through Anatop filter 0.020 µm pore size)

Sample name	Hydrodynamic diameter (nm)
Polymer 30 min 1st	1.860
Polymer 30 min 2nd	1.509
Polymer 30 min 3rd	1.610

Figure S6A: DLS characterization of ionomer after 30 min of growth or 25% conversion. Hydrodynamic effective diameter analyzed from three runs. Three syntheses with the same work up were measured. All data shown.
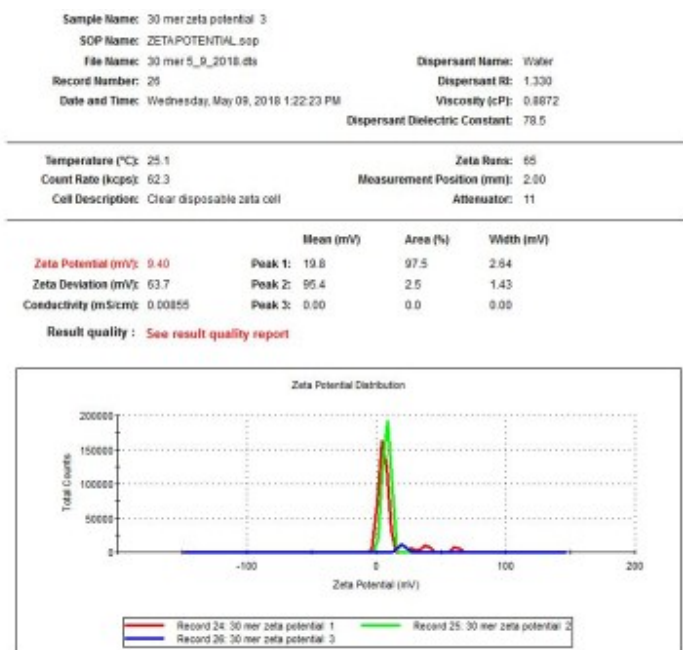

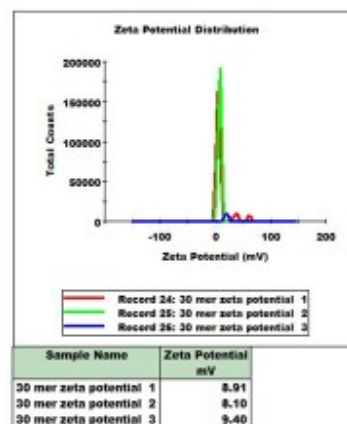**Figure : Zeta potential of polymer grown for 30 minutes (sample is centrifuged and dialyzed**

Sample Name	Zeta Potential mV
30 mer zeta potential 1	8.91
30 mer zeta potential 2	8.10
30 mer zeta potential 3	9.40

Figure S6B: Zeta potential characterization of ionomer after 30 min of growth or 25% conversion. Average zeta potential is 8.8 mV. All data shown.
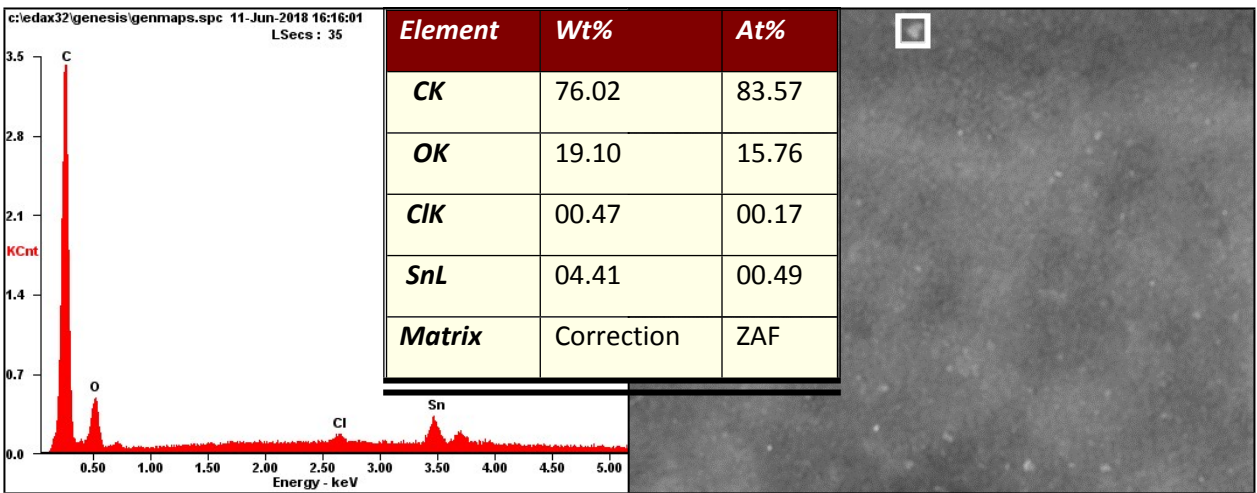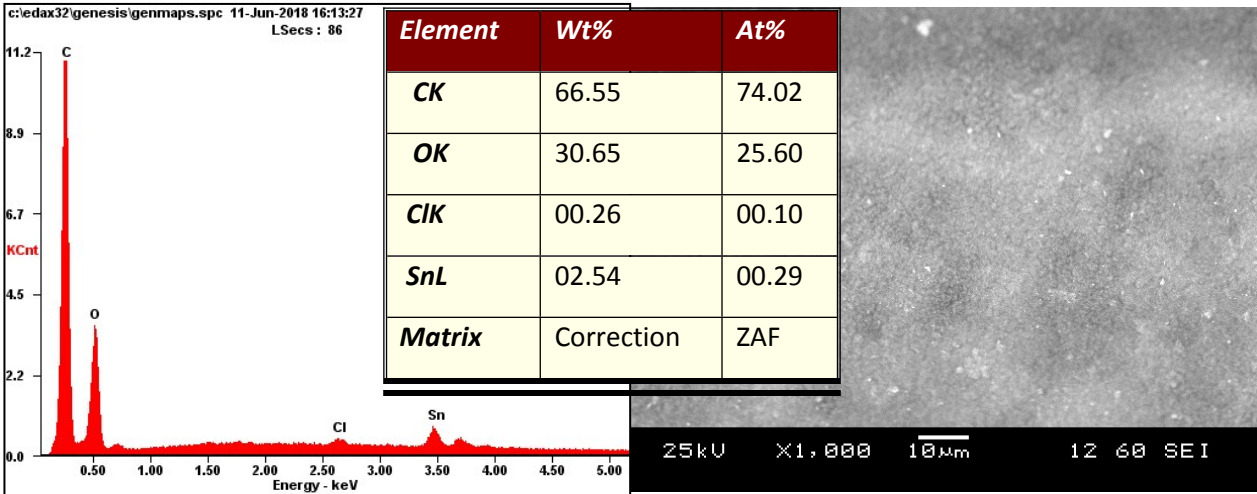
Figure S7: EDX of 2 h **Aq-SNR** thin film on MCE membrane. Small particles of tin compound still present after acid treatment. Could be tin(IV) oxide. Both images acquired at 25kV with the same 10 μm scale bar as shown in upper image. Lower data is of the small area in the box surrounding a particle. Sn concentration is twice as high on that spot indicating that persistence of insoluble tin(IV) oxide.
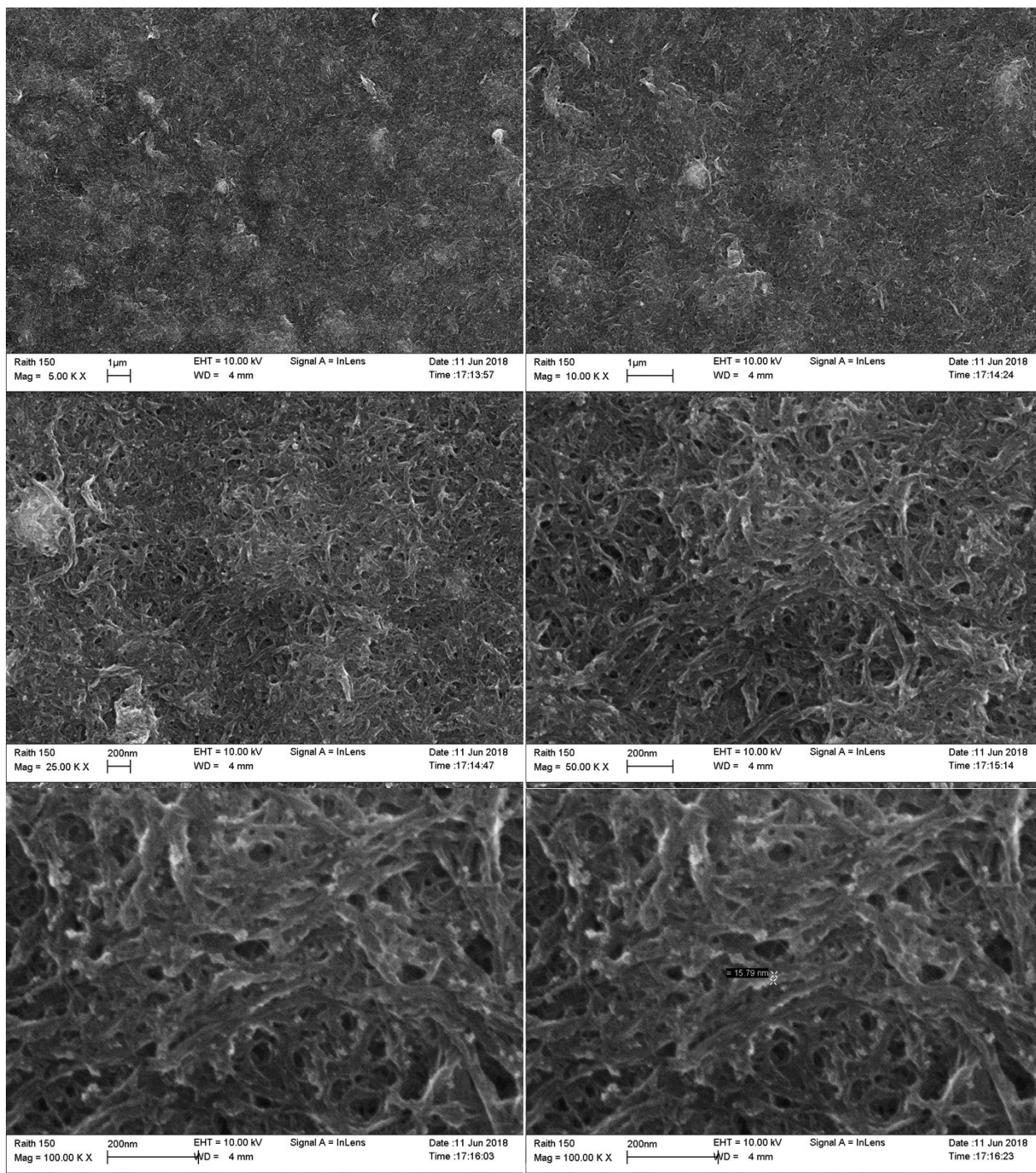
Figure S8: FE-SEM micrographs of **Aq-SNR** thin film on top of an MCE membrane. Pin hole free, smooth films were made with areas up to 16 cm². Scale up to large area membranes is beyond the scope of this proof of principle study.
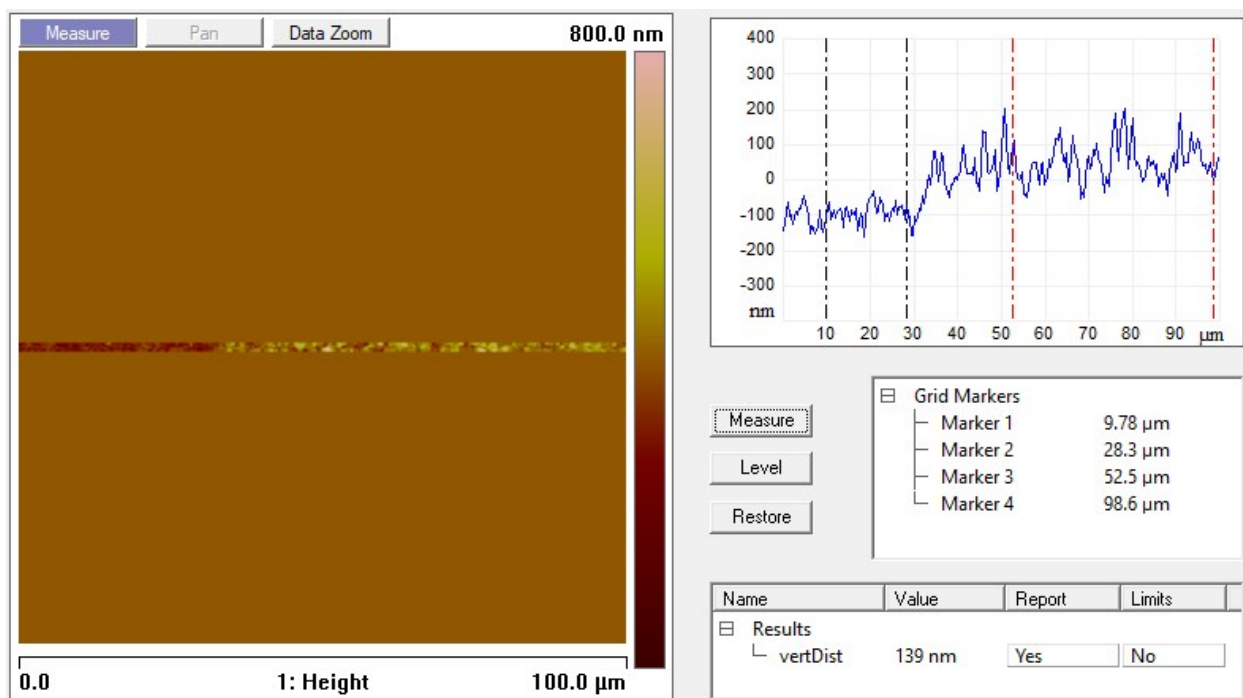
Figure S9: AFM micrographs of **Aq-SNR** thin film on top of an MCE membrane. Cross sectional analysis shows about a 140nm thick film. The AFM tip seems to be interacting strongly with the ionomer film. These films are not completely dry.

Covalent attachment analysis

Functionalization time	Ratio Total mass / SWCNTs mass
2 h	2.40
12 h	3.73
3 days	4.80 supernatant only

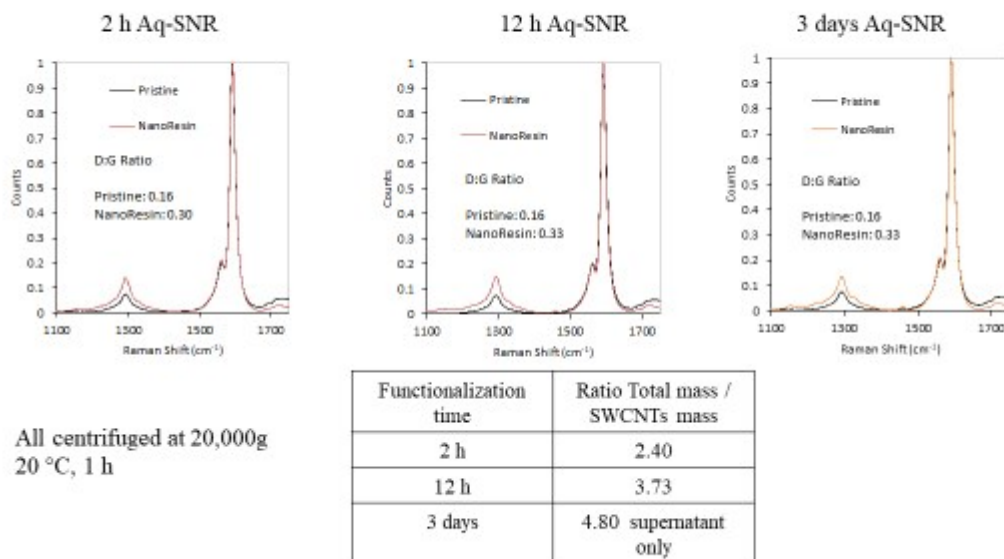All centrifuged at 20,000g
20 °C, 1 h

Figure S10A: Baseline-Normalized Raman spectra of Pristine SWCNT compared to: 2h (left), 12h (center), and 3 day (right) **Aq-SNR** after centrifugation at 20,000 RCF for 1 hr. Increase in the ratio of the area under the D and G bands (the D:G ratio) indicates covalent functionalization of ionomer strands to SWCNT wall. Total mass of **Aq-SNR** to SWCNT mass shown in table.
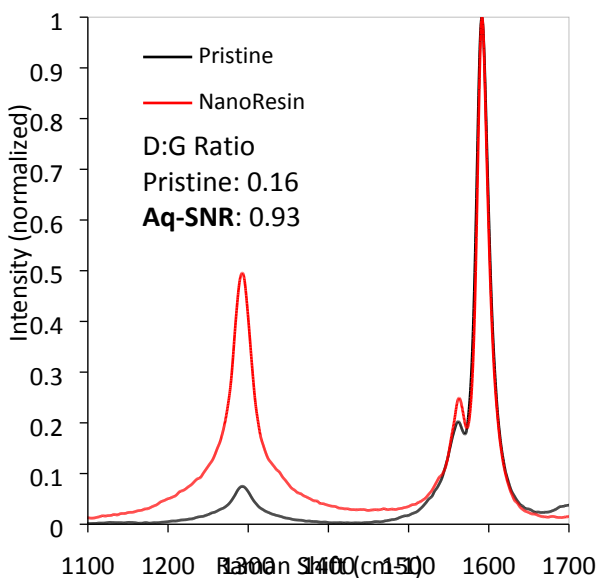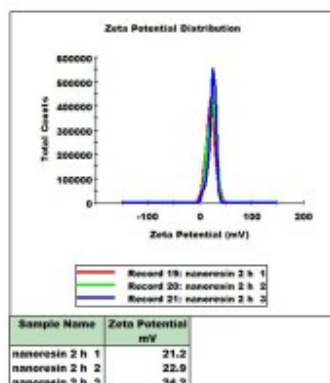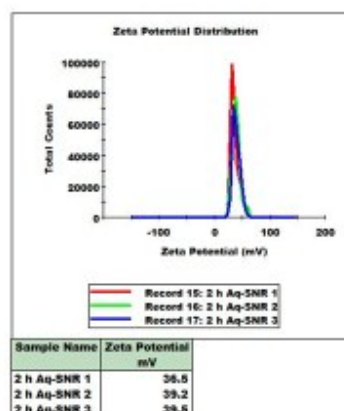

Figure S10B: Baseline-Normalized Raman spectra of Pristine SWCNT and 3 day **Aq-SNR** after centrifugation at 200,000 RCF for 1 hr. Increase in the ratio of the area under the D and G bands (the D:G ratio) indicates covalent functionalization of ionomer strands to SWCNT wall.

DLS/Zeta analysis

Before centrifugation

After centrifugation at 20,000 g

# DLS/Zeta analysis
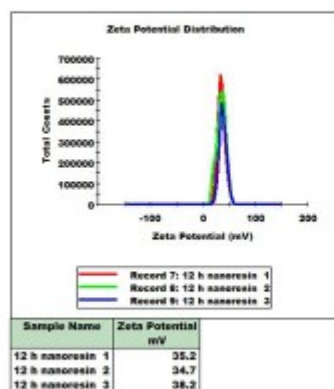
Before centrifugation
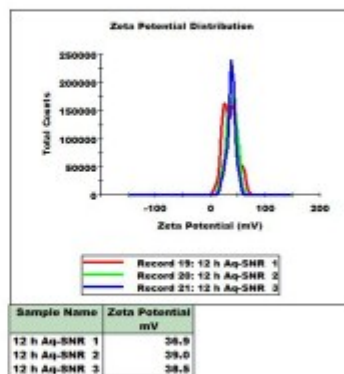
After centrifugation at 20,000 g

Figure S11: Zeta potential data for 2h (top) and 12 h (bottom) functionalized **Aq-SNR**. Material from the supernatant after a 20,000 g centrifugation exhibit a more stable dispersion and higher zeta potential. All Zeta potentials were calculated from the measured electrophoretic mobility using the Smoluchowski model.

DLS/Zeta analysis

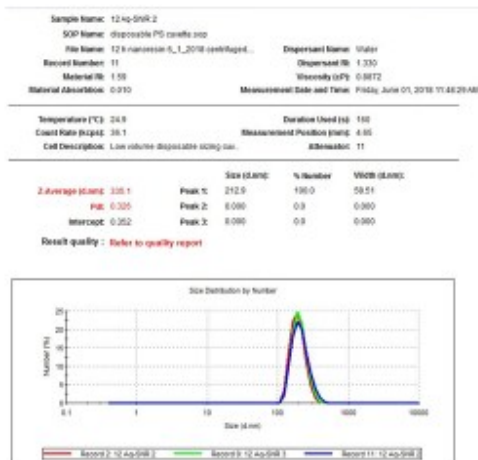

Number distributions of 2h Aq-SNR
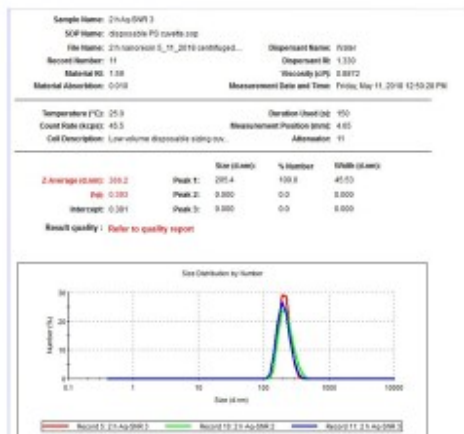
Sample name	Hydrodynamic diameter (nm)
2 Aq-SNR 1st	210.8
2 h Aq-SNR 2nd	224.0
2 h Aq-SNR 3rd	205.4

Centrifuged at 20,000g

Avg ± standard error: 213.4 ± 5.520 nm

Number distributions of 12h Aq-SNR

Sample name	Hydrodynamic diameter (nm)
12 Aq-SNR 1st	196.5
12 h Aq-SNR 2nd	205.9
12 h Aq-SNR 3rd	212.9

Centrifuged at 20,000g

Avg ± standard error: 205.1 ± 4.750 nm

Number distributions of 3 days Aq-SNR
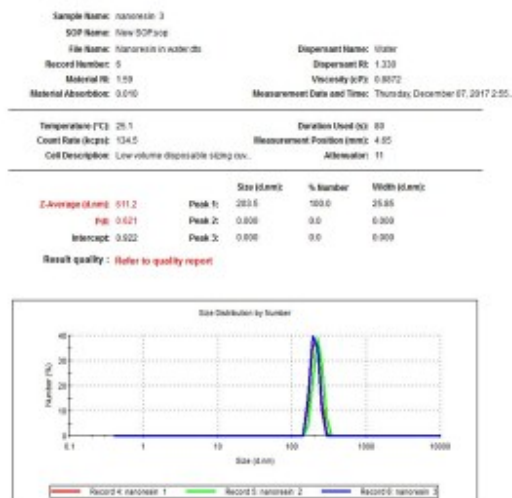
Sample name	Hydrodynamic diameter (nm)
3 days Aq-SNR 1st	208.6
3 days Aq-SNR 2nd	226.8
3 days Aq-SNR 3rd	203.5

Centrifuged at 20,000g

Avg ± standard error: 213.0 ± 7.070 nm

Figure S12: DLS data for 2h (top), 12 h (middle) and 3 day (bottom) functionalized **Aq-SNR**. Material from the supernatant after a 20,000 g centrifugation are consistent with a flexible rod model.

Comparisons of NanoResins

NanoResin	Q (in terms of SWCNTs mass)
2 h	99.06
12 h	97.45

NanoResin	Q (in terms of SWCNTs mass)
2 h	105.5
12 h	100.1

NanoResin	Q (in terms of SWCNTs mass)
2 h	101.0
12 h	105.2

NanoResin	Q (in terms of SWCNTs mass)
2 h	100.9
12 h	101.9

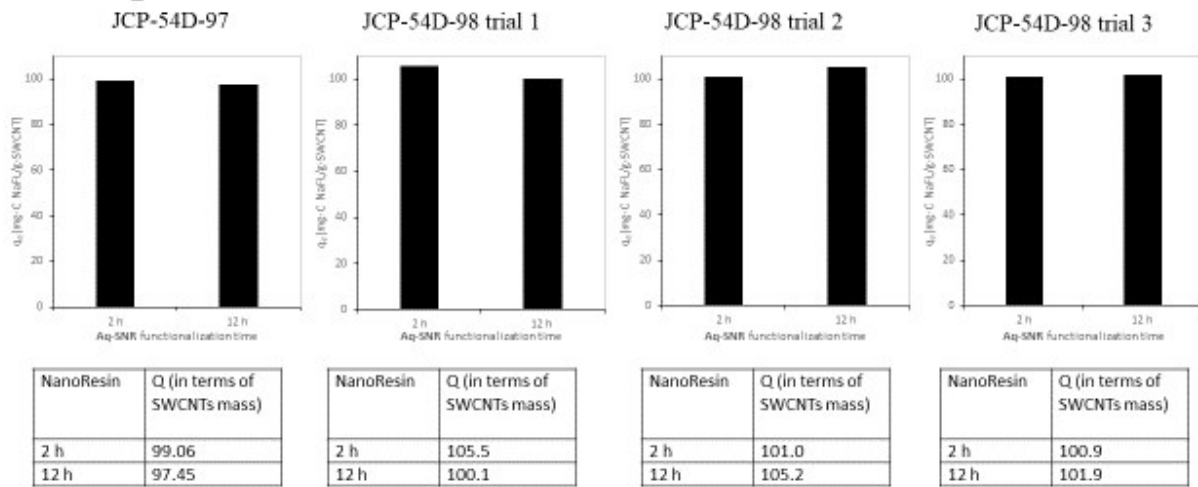**Figure S13**: Equilibrium loading capacity of NaFL onto Aq-SNR using an initial concentration C_o = 5.8 mg-C / L. The mass of the adsorbent is the SWCNT mass only so we can directly compare the material based on number of nanotubes in the film. Value of q_e listed in tables.

Table S1: Adsorption of various analytes onto **Aq-SNR** thin films.

Adsorbate	Initial Conc. C_i (mg-C/L)	Final Conc. C_f (mg-C/L)	Adsorbate Volume (mL)	Mass of Adsorbate removed (mg)	Mass of Adsorbent (NanoResin) (mg)	q (mg-C adsorbate / g adsorbent)
NaFL	5.49	3.79	3.00	5.11×10^{-3}	0.17	30.1
PFOA	4.31	1.82	3.00	7.47×10^{-3}	0.17	43.9
PFOS	5.07	1.41	3.00	1.09×10^{-2}	0.17	64.6
Tetracycline hydrochloride	4.35	3.85	3.00	1.50×10^{-3}	0.17	8.82
Carbenicillin disodium	6.67	3.42	3.00	9.77×10^{-3}	0.17	57.5
Bromoacetic acid	3.41	1.87	3.00	4.65×10^{-3}	0.17	27.3
Chloroacetic acid	2.54	1.80	3.00	2.22×10^{-3}	0.17	13.1
Bentazon	6.81	3.93	3.00	8.66×10^{-3}	0.17	50.9
Terbacil	6.15	4.65	3.00	4.50×10^{-3}	0.17	26.5
Bromacil	5.55	3.90	3.00	4.95×10^{-3}	0.17	29.1