Supplementary Information

Feasibility of Graphene-Polymer Composite Membranes for Forward Osmosis Applications

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In the case of method N1, N2 and N3 (*Fig. S.1*) graphene dispersions were prepared by using an ultrasonic probe. Graphite was directly mixed with 80 mL NMP solvent (5 mg/mL). Then, this mixture was exposed to sonication for 4 h at 60% amplitude in an ice-cooled water bath. Here, two different centrifugation rotation speeds were applied to see the effects of using various speeds on flake size and thickness. Dispersions were placed into centrifugation for 45 minutes with 1500 rpm (method N1) and 4500 rpm (method N2). Then, the top 85% of supernatants from each set of experiments were collected for further analysis and the sediment was discarded. Dispersion N2 was exposed to further centrifugation for 45 minutes with 4500 rpm and the top 85% of supernatant was collected and labelled as N3.

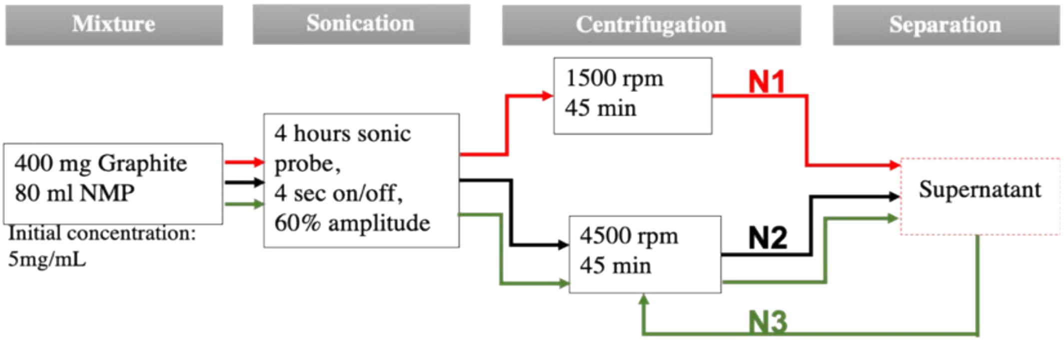


Figure S.1. Schematic description of fabrication of graphene dispersion via methods N1 (red arrows), N2 (black arrows) and N3 (green arrows).

In the case of method E1 (*Fig. S.2*), graphite flakes were mixed with potassium sodium tartrate $KNaC_4H_4O_6.4H_2O$ with a weight ratio of 1:3 and ethanol (10 mg/mL initial concentration of graphite and 30 mg/mL concentration of salt). This mixture was then exposed to sonication for 4 hours via ultrasonic bath with a frequency of 45 kHz, keeping the bath's temperature as room temperature by changing the water every 30 minutes. After completing sonication, since the resultant dispersion had a broad flake size distribution (highly poly-dispersed) and also included salt in the solution, the centrifugation process was applied to separate large unexfoliated graphitic-like structures from the dispersion in order to have smaller thinner flakes in the dispersion. Next, the mixture was placed into centrifugation for 30 minutes with 3000 rpm. Then, the top 85% of supernatant was collected for further analysis and the sediment was discarded. The supernatant was washed with water several times to remove possible salt residuals and re-dispersed in the same amount of ethanol for about 1 hour. In the end, dispersion E1 was obtained. Furthermore, E1 was exposed to another centrifugation for 30 minutes with 3000 rpm (*Fig. S.2*). The supernatant was gathered from this and labelled as the dispersion E2, which was used to prepare graphene-based membranes.

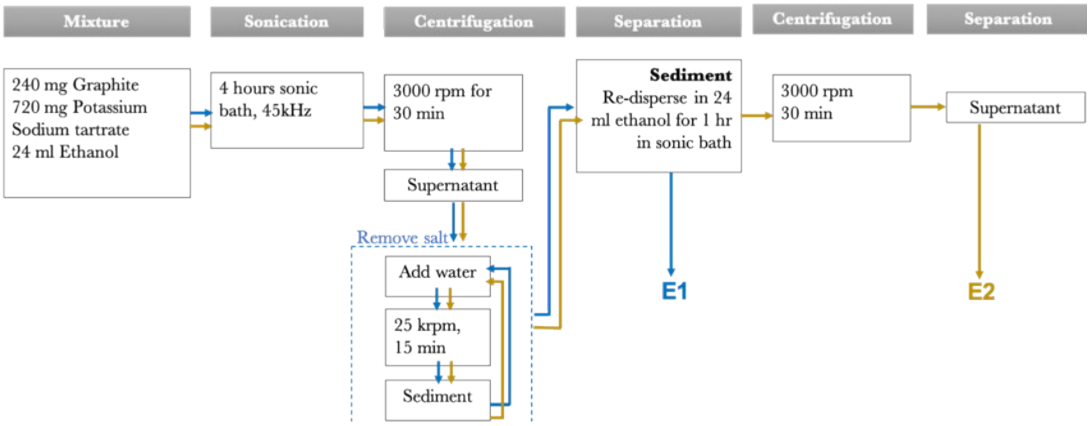
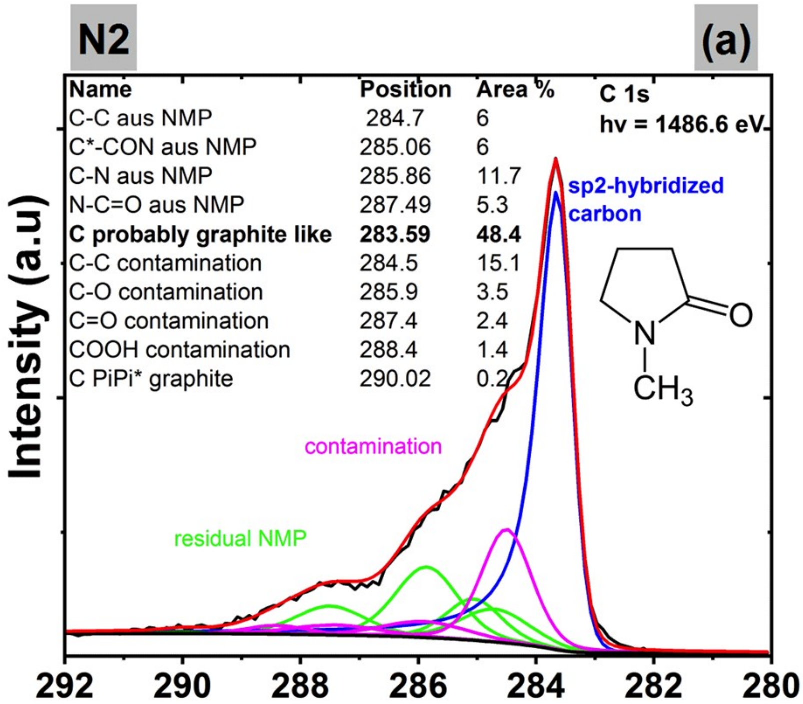


Figure S.2. Schematic description of fabrication of graphene dispersion via methods E1 (blue arrows) and E2 (yellow arrows).



Name	Position	Area %
C-C aus NMP	284.7	6
C*-CON aus NMP	285.06	6
C-N aus NMP	285.86	11.7
N-C=O aus NMP	287.49	5.3
C probably graphite like	**283.59**	**48.4**
C-C contamination	284.5	15.1
C-O contamination	285.9	3.5
C=O contamination	287.4	2.4
COOH contamination	288.4	1.4
C PiPi* graphite	290.02	0.2

Figure S.3 XPS analysis of graphene dispersion in NMP via procedure N2 (a). Contribution of the components used in fitting of C 1S peak is also listed in the graph. Strong NMP residual was observed on the substrate.

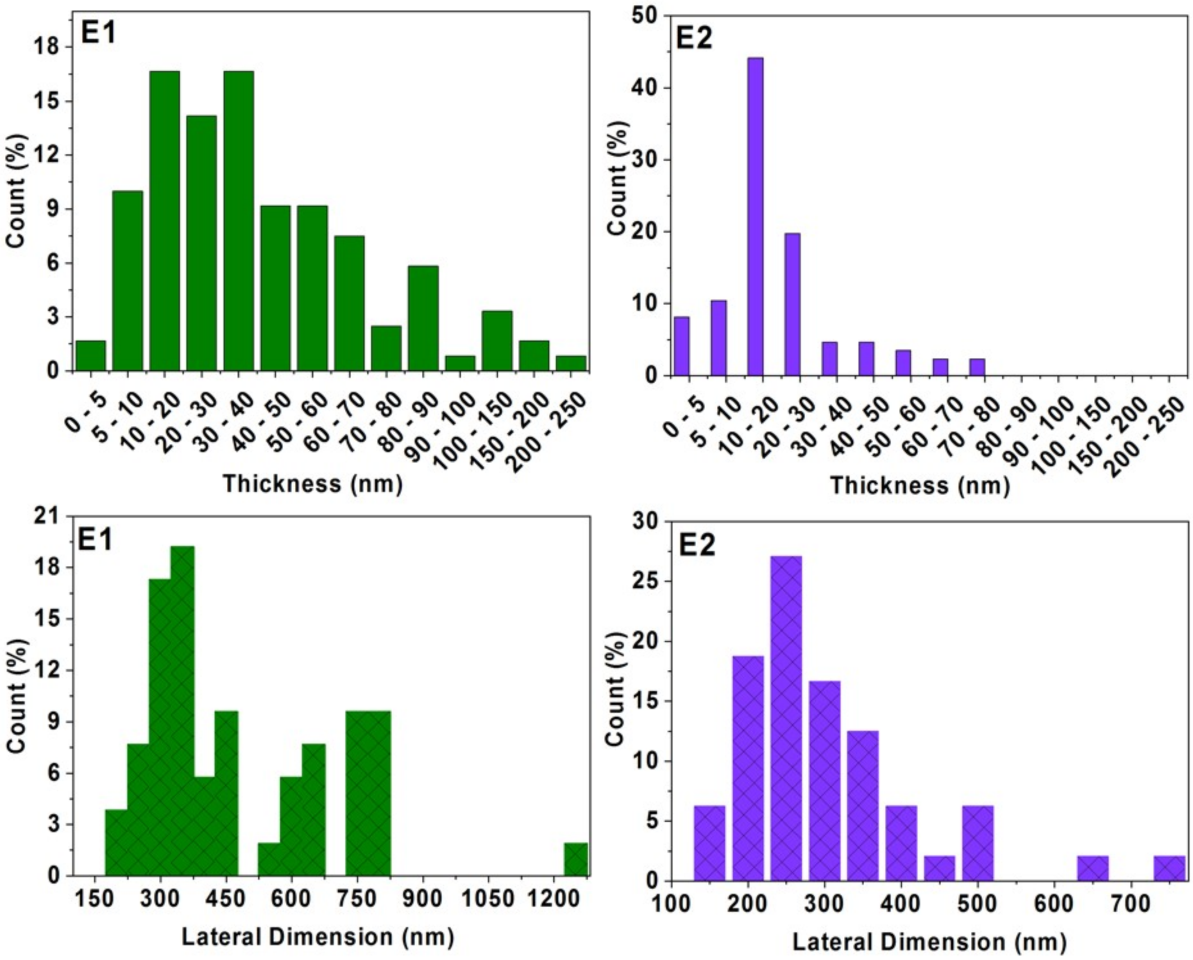


Figure S.4 AFM thickness and lateral flake size histograms of graphene dispersion in ethanol via procedure E1 (left, green) and E2 (right, purple).

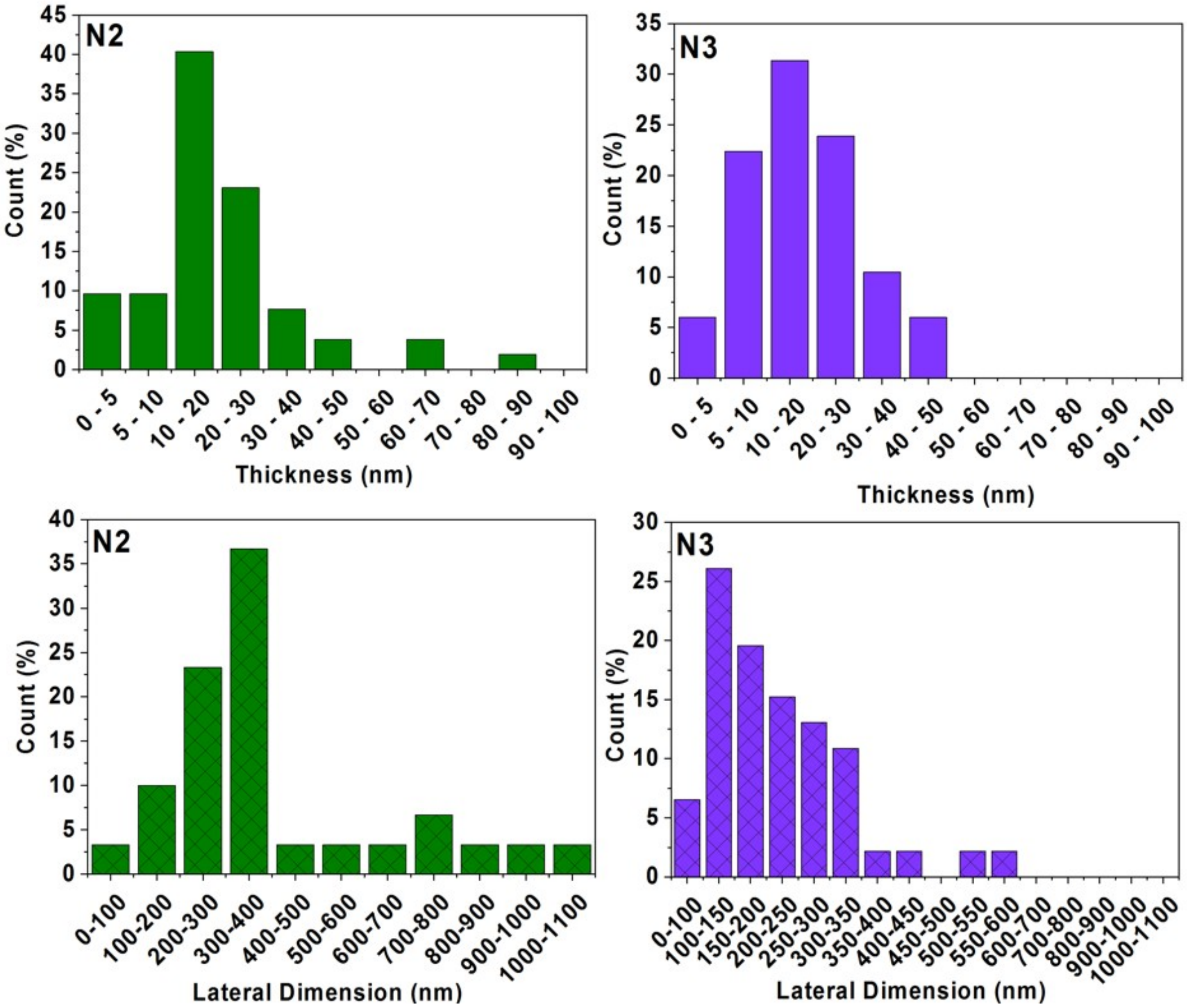


Figure S.5 AFM thickness and lateral flake size histograms of graphene dispersion in NMP via procedure N2 (left, green) and N3 (right, purple).

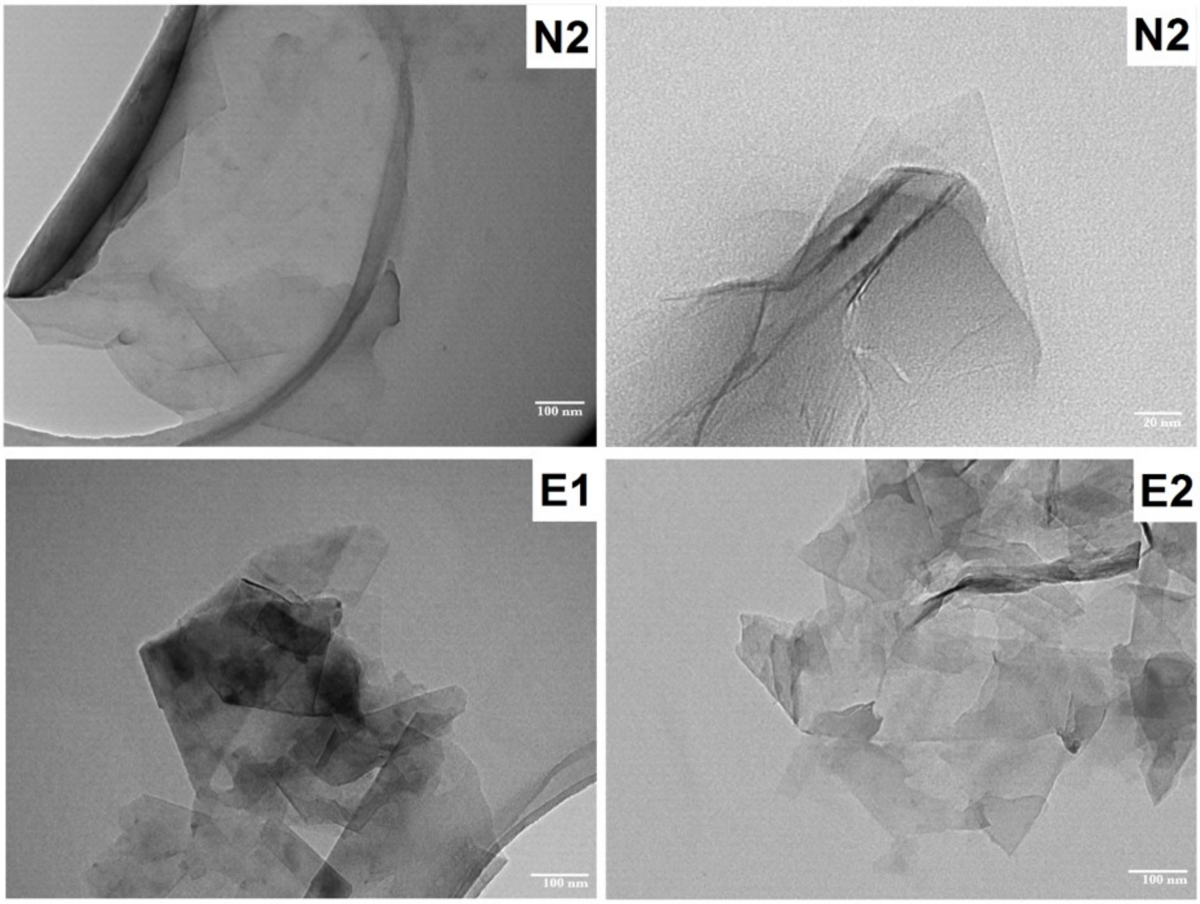


Figure S.6 TEM images of dispersion of N2, E1 and E2.

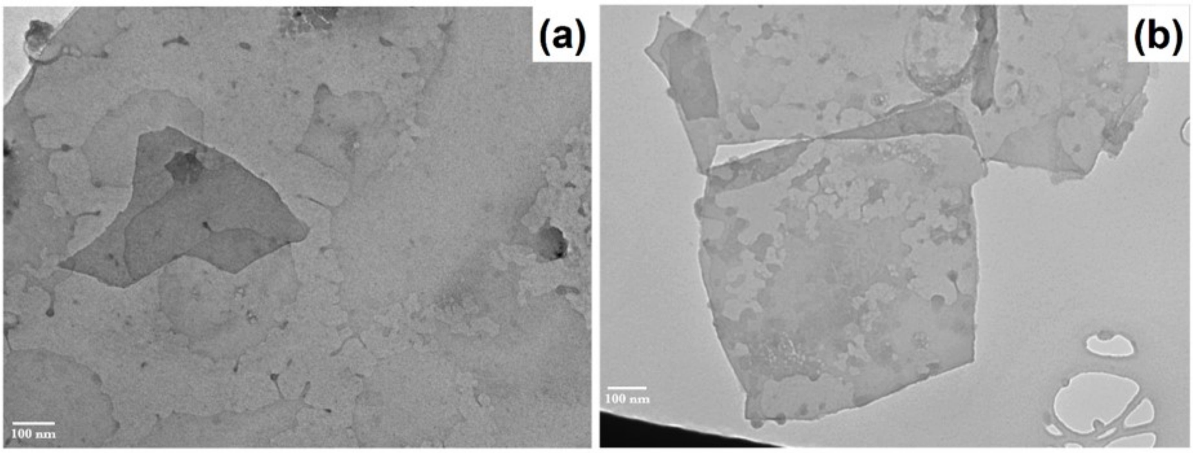


Figure S.7 TEM images of graphene dispersion fabricated via method N3.

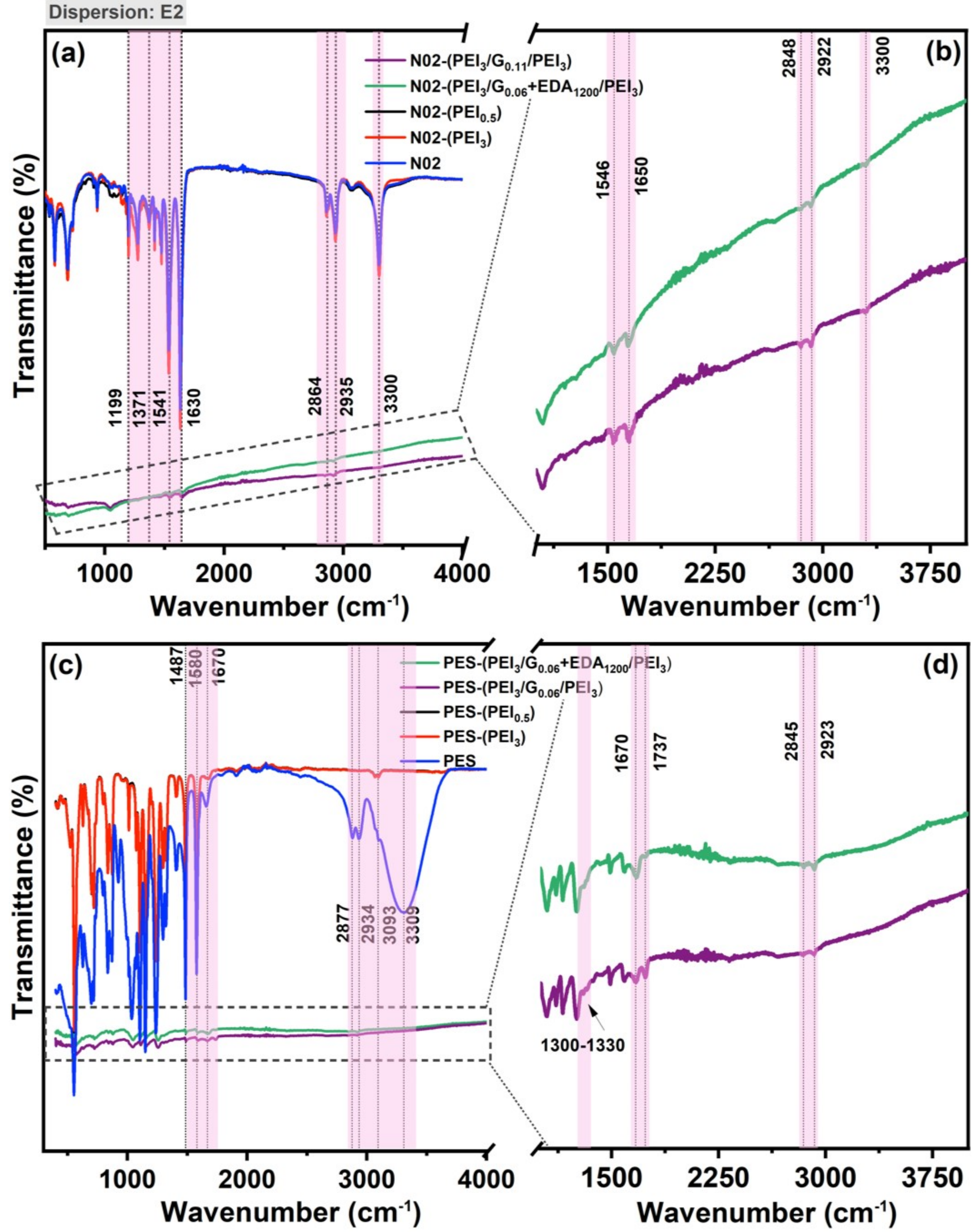
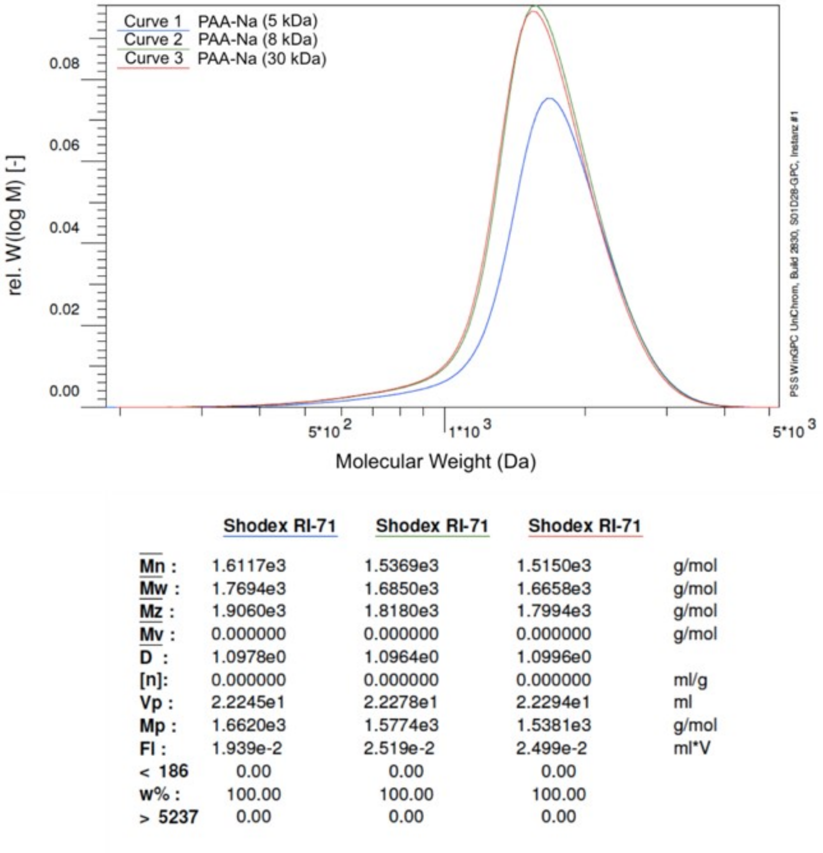


Figure S.8. FTIR spectra of an unmodified Nylon membrane and various concentrations of PEI modified Nylon membranes and Graphene-Polymer/Nylon composite membranes (a and b (enlarged version of composite membranes)), unmodified PES membrane and various concentration of PEI modified PES membranes and Graphene-Polymer/PES hybrid membranes (c and d (enlarged version of composite membranes)).

In *Fig. S.8a*, characteristic peaks for Nylon appears around 2935 cm-1, 1371 cm-1, and 1199 cm-1 due to CH2 stretching, C-N stretching + in-plane N-H deformation, an amide III band and an amide III band coupled with the hydrocarbon skeleton, respectively. The peak observed at 1630 cm-1 is attributed to the amide I band and a carbonyl stretching vibration in the Nylon unit. The peak at 1541 cm-1 appears due to the amide II band and CH2 asymmetric deformation. *Fig. S.8b* shows the enlarged spectrum which contains very weak peaks, centred at almost same wavelength compared to unmodified Nylon membrane.

The unmodified PES membrane (*Fig. S.8c*) provides the following vibration peaks; hydroxyl groups -OH stretching vibration at 3309 cm-1, C-H stretching at 2877 and 2934 cm-1, the peak at 1670 cm-1 can be attributed to the carbonyl group (C=O) of amide groups, the peaks around 1487 cm-1 and 1580 cm-1 are C=C stretching in aromatic ring, the peaks at 1170 cm-1 and 1230 cm-1 are due to S=O stretching of PES aromatic rings. -OH stretching vibration at 3309 cm-1 and asymmetric and symmetric stretching of C-H at 2934 cm-1 and 2877 cm-1 disappeared when PEI is introduced to the membrane surface. Since these aliphatic peaks do not belong to PES, they might have been caused by the water in the membrane which was probably not completely dry. The peaks could also have been caused by the fact that there might have been PVP which binds to water. So, probably the spectrum has been taken for an unmodified membrane which may not have been completely depleted of the additional substances, they were still in the membrane as received, and later these additional substances have been washed out when composite membranes were prepared. *Fig. S.8d*, illustrates the enlarged spectrum of the graphene-polymer/PES hybrid membranes. C-H vibration stretching can be seen at 2845 cm-1 and 2923 cm-1, the carbonyl group (C=O) peak at 1670 cm-1 is found in all membranes. However, extra peak at 1737 cm-1 and 1300-1330 cm-1 appears in the case of PEI modified graphene membranes due to C=O stretching. These peaks are not observed in cross-linker modified graphene-polymer hybrid membrane cases.



	Shodex RI-71	Shodex RI-71	Shodex RI-71	
$\overline{Mn}$:	1.6117e3	1.5369e3	1.5150e3	g/mol
$\overline{Mw}$:	1.7694e3	1.6850e3	1.6658e3	g/mol
$\overline{Mz}$:	1.9060e3	1.8180e3	1.7994e3	g/mol
$\overline{Mv}$:	0.000000	0.000000	0.000000	g/mol
D :	1.0978e0	1.0964e0	1.0996e0	
[n]:	0.000000	0.000000	0.000000	ml/g
Vp :	2.2245e1	2.2278e1	2.2294e1	ml
Mp :	1.6620e3	1.5774e3	1.5381e3	g/mol
FI :	1.939e-2	2.519e-2	2.499e-2	ml*V
< 186	0.00	0.00	0.00	
w% :	100.00	100.00	100.00	
> 5237	0.00	0.00	0.00	

Figure S.9. Gel permeation chromatography (GPC) analysis of PAA-Na solution prepared by using 5 kDa, 8 kDa and 30 kDa molecular weights.

Gel permeation chromatography (GPC, *Fig. S.9*) analysis was additionally employed to investigate the actual average molecular weight distribution of polyelectrolytes. The results expectedly reveal that molecular weight distribution of all three PAA-Na are almost identical (5 kDa → 1.61 kDa; 8 kDa → 1.54 kDa; 30 kDa → 1.51 kDa)