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### **Paper:**

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## Supplementary Material

### **Polyvinylidene fluoride membranes impregnated at optimised content of pristine and functionalised multi-walled carbon nanotubes for improved water permeation, solute rejection and mechanical properties**

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#### **1. Dispersion of CNTs - Method**

50mL of solvent DMF or NMP were transferred into 70mL clean capped bottles followed by adding 10mg CNTs (i.e. CNTs-O or CNTs-P) into each of the bottles. Once the caps were tightly closed, the bottles were shaken for 1 minute to pre-distribute the CNTs and then followed by ultrasonication for 1 hour in a 38 kHz ultrasonic bath (Kerry Pulsatron, Guyson International, Ltd. UK). The ultrasonication time was divided into 4 steps (15 min each) separated by cooling (5 min) between steps to prevent water temperature exceeding 30°C since high temperatures reduce the dispersion of CNTs [1]. The dispersed CNT solutions were analysed for their dispersion stabilities by following the settling times of the CNTs. The solvent that gave the least CNT settling, hence stable dispersion, was selected for the fabrication of the membranes. As discussed further in the results, NMP solvent was selected in this study.

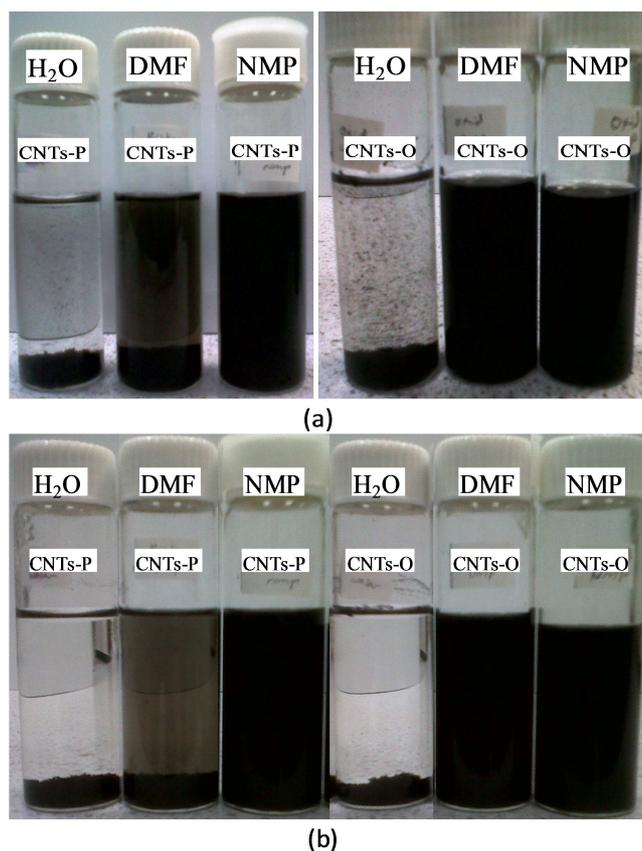
## 2. Dispersion of CNTs – Results

Due to their strong surface energy and high aspect ratio, CNTs tend to form agglomerations and entanglements, which make their dispersion in solution difficult. In fact, a bundle state of two parallel CNTs is far more stable than a pair of isolated CNTs. Moreover, free energy barrier between bundles and isolated tubes is so high for micron lengths [2] which makes the dispersion of CNTs difficult. In this study, the dispersion performance of pristine and oxidised CNTs in common membrane fabrication solvents DMF and NMP was studied hence a suitable solvent could be chosen. In addition, dispersion of CNTs in water was also made for comparison only.

Visual images of the dispersions (Figure S1) showed that most of the dispersed CNTs in water precipitated after 1 hour with complete precipitation after 3 hours (results are not shown) whilst better dispersion stability was observed in DMF and NMP even after one week from sample preparation. Comparing DMF to NMP, Figure S1 shows that CNT dispersions were more stable in NMP than DMF. The three solvents could be classified in terms of CNT dispersion stability as  $\text{NMP} > \text{DMF} \gg \text{water}$ . Besides, comparing the stability of CNTs-P and CNTs-O in NMP, it was difficult to make such a comparison by simple visual observation since both dispersions have almost the same visible darkness level. Hence, particle size measurements after 1h and 72h of preparation were made. It was found that the cumulative particle size distribution (results are not shown) has changed between 1h and 72h by only a little (<5%) indicating that both CNT types presented similar dispersion stability in NMP.

DMF and NMP are polar aprotic solvents where they have H or O atoms in their chemical structure but lack H–O or N–H bonds. In contrast, water which is a polar protic solvent is rich

in H–O bonds. DMF and NMP have high values for hydrogen bond acceptance basicity ( $\beta$ ), negligible values for hydrogen bond donation ( $\alpha$ ), and high values for solvatochromic parameter ( $\pi^*$ ). These properties make DMF and NMP good dispersing solvents for CNTs [3]. Among the two solvents, NMP has the best dispersion capability since it has higher solvatochromic parameter of 0.92 as compared to that of DMF of 0.88 [4]. However, despite water having solvatochromic parameter value higher than NMP of 1.09, its performance in dispersing CNTs is far less favourable since water has high hydrogen donating ability [5]. Furthermore, NMP presents the highest dispersive solubility parameter,  $18.0 \text{ MPa}^{0.5}$ , as compared to  $17.4$  and  $15.6 \text{ MPa}^{0.5}$  for DMF and water respectively [6], which also supports its superior property for dispersing CNTs.

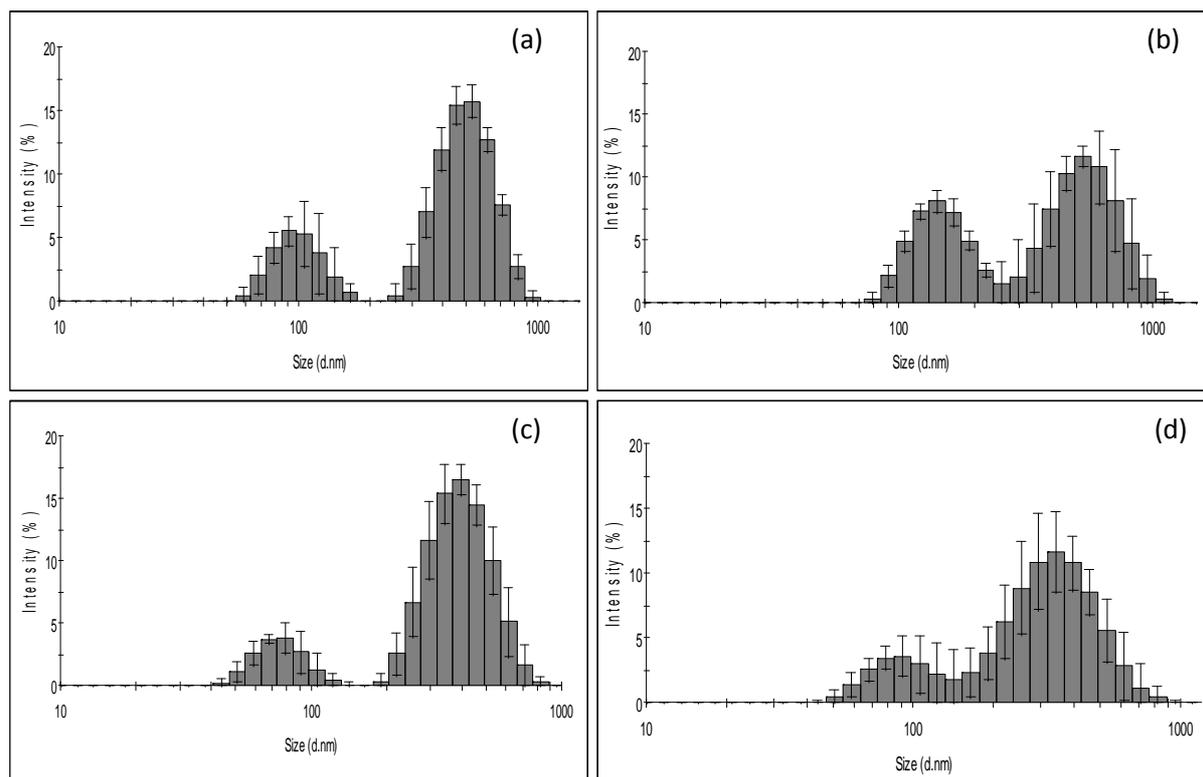


**Figure S1:** Images of 0.02% CNT dispersion in different solvents (a) 1 hour settlement and (b) 1 week settlement.

Since NMP presented excellent dispersion abilities of both pristine and oxidised CNTs, it was chosen for the fabrication of the membranes in this study.

*a. Particle size distribution of CNTs in NMP*

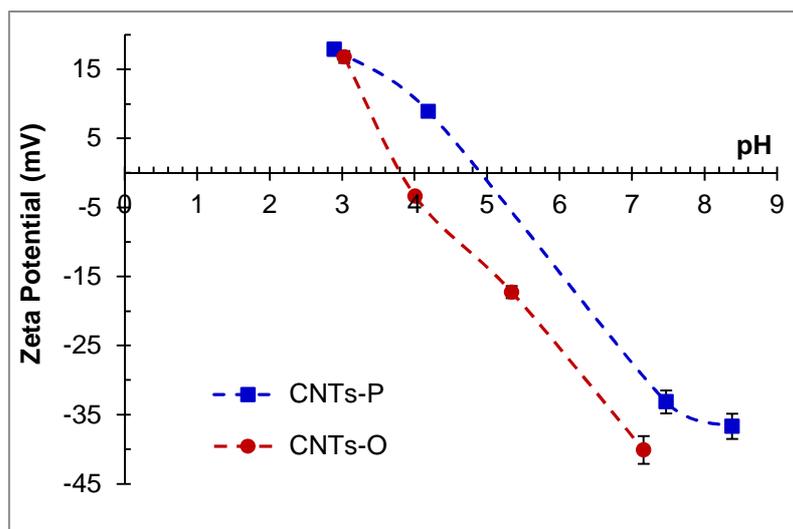
Particle size distributions in NMP were determined for both CNTs-O and CNTs-P and the results are shown in Figure S2. Figures S2a-d show bimodal particle size distributions with maximum peak particle intensities of 91 nm and 531 nm for CNTs-P and of 79 nm and 396 nm for CNTs-O after 1 hour from stopping mixing with ultrasonication. These maximum peaks have shifted after 72 hour to 142 nm and 531 nm for CNTs-P with new agglomerate formation occurring at 1110 nm. Similarly, the maximum peaks have also shifted to 91 nm and 348 nm for CNTs-O with the formation of new agglomerated particles at a size of 955 nm. This indicates that there was a modest agglomeration of both types of CNTs. Considering the overall average particle sizes for CNTs-P and CNTs-O after 1 hour and 72 hour from stopping ultrasonication, they have slightly increased due to agglomeration from about 366 nm and 327 nm to about 374 nm and 337 nm for CNTs-P and CNTs-O respectively. The appearance of new agglomerations with larger particle sizes after stopping ultrasonication is likely resulting from particles bundling together by van der Waals interactions [7]. Moreover, high aspect ratio, high surface energy, and hydrophobic properties of CNTs encourage the particles to agglomerate. The cumulative particle size distribution (results are not shown) shows that most of the CNTs-O particles were distributed in the particle size region between 200 – 800 nm whilst CNTs-P were distributed at about 300 – 900 nm which indicates that slightly smaller particles of CNTs-O were dispersed in NMP as compared to CNTs-P. Modification of CNT surface by oxygen plasma have introduced oxygenated functional groups (e.g. -C=O, -COOH and -OH) which increase the dipole-dipole interaction between the surface of the modified CNTs and polar solvents [8] hence improved the dispersability of CNTs in those polar solvents [9].



**Figure S2:** Particle size distribution of CNTs in NMP after 1hour (CNTs-P (a), CNTs-O (c)) and after 72 hour (CNTs-P (b), CNTs-O (d)) from stopping ultrasonication.

### *b. Zeta potential of CNTs*

Figure S3 shows the change of zeta potential of CNTs-P and CNTs-O as function of pH. According to Figure S3, similar positive zeta potentials at pH 3 was obtained for both CNTs but a further increase to pH 4 resulted in a drop of CNTs-O's zeta potential to a negative value from about 16.8 to -3.4 mV whilst CNTs-P's zeta potential dropped slightly from about 17.5 to 9.0 mV. The isoelectric values were obtained at pH 3.8 for CNTs-O and shifted to pH 4.7 for CNTs-P. Further pH increase resulted in CNTs having more electronegative charges, as also observed by other studies [10, 11]. Figure S3 also shows that at all pHs, CNTs-O were more negatively charged as compared to CNTs-P. For example, the zeta potential of CNTs-O at pH 7 is about -40 mV whilst for CNTs-P is about -35 mV. This is consistent with the fact that CNTs-O have more electronegative charge than CNTs-P resulting from deprotonated oxidised functional groups including  $-C=O$ ,  $-COOH$  and  $-OH$  on the CNTs-O surface [12].



**Figure S3:** Zeta potential of pristine and plasma oxidised CNTs as function of pH.

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