**Supporting Information**

# Antifouling behaviours of PVDF/nano-$TiO_2$ composite membranes revealed by surface energetics and quartz crystal microbalance monitoring

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**Contents**



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## Calculation of XDLVO theory

In order to obtain the interfacial energy, surface tension parameters ($\gamma_s^{LW}$, $\gamma_s^{+}$, $\gamma_s^{-}$) of the membrane and alginate must be determined by performing contact angle measurements using three probe liquids with known surface tension parameters and employing the extended Young's equation.[1] Two of them should be polar and one should be apolar. The probe liquids used in this study are ultrapure water, formamide and diiodomethane, and the surface tension parameters of the three probe liquids are shown in Table S1. The formamide and diiodomethane were obtained from Sinopharm (Shanghai, China). Ultrapure water was obtained from a Millipore water purification system.

Table S1 Surface tension parameters (mJ/m$^2$) of probe liquids[2]

| | $\gamma_s^{LW}$ | $\gamma_s^{+}$ | $\gamma_s^{-}$ | $\gamma^{AB}$ | $\gamma^{TOT}$ |
|---|---|---|---|---|---|
| Ultrapure water | 21.8 | 25.5 | 25.5 | 51 | 72.8 |
| Diiodomethane | 50.8 | 0 | 0 | 0 | 50.8 |
| Formamide | 39 | 2.3 | 39.6 | 19 | 58 |

The contact angle of all three probe liquids and each membrane (or alginate) was measured by an optical contact angle measurement system (OCA 15 Plus, Data physics GmbH, Germany). The details procedure of contact angle measurement was presented in our previous report.[3] At least four measurements at different locations were averaged to obtain contact angle for each sample. The contact angle measurement results are shown in Table S2.

Table S2 Contact angles between probe liquids and membrane/alginate (º)

| | T-0 | T-0.02 | T-0.05 | T-0.1 | T-0.5 | Alginate [a] |
|---|---|---|---|---|---|---|
| Ultrapure water | 86.1±3.2 | 75.5±3.2 | 73.7±4.0 | 76.9±2.1 | 72.0±3.1 | 79.8±4.3 |
| Diiodomethane | 61.3±3.5 | 56.5±1.1 | 50.2±3.1 | 55.8±2.0 | 51.6±2.1 | 47.46±3.8 |
| Formamide | 67.0±2.2 | 61.6±3.6 | 59.3±4.0 | 60.7±2.6 | 50.1±0.7 | 52.3±0.5 |

[a] ionic strength=10 mM, pH=6.5

The surface tension parameters of each probe liquid and their relative contact angle value between the probe liquid and membrane (or alginate) was substituted into Eq.(7) and $\gamma_s^{LW}$, $\gamma_s^{+}$, and $\gamma_s^{-}$ of the membrane was obtained by solving the equations. Then, $\gamma_s^{AB}$, and $\gamma_s^{TOT}$ could be obtained according to Eqs. (8) and (9). Subsequently, we calculated $\Delta G_{h_0}^{LW}$ and $\Delta G_{h_0}^{AB}$ of all the membranes by using Eqs. (5) and (6), respectively, as shown in Table 1. The surface tension parameters and free energy of cohesion of alginate solution with 10 mM NaCl concentration under pH=6.5 were shown in Table S3 in order to calculate the total interfacial energy versus separation distance between alginate and different membranes.

Table S3 Surface tension parameters and free energy of cohesion of alginate (Unit: mJ/m$^2$)[a]

| | $\gamma_s^{LW}$ | $\gamma_s^{+}$ | $\gamma_s^{-}$ | $\gamma^{AB}$ | $\gamma^{TOT}$ | $\Delta G_{h_0}^{LW}$ | $\Delta G_{h_0}^{AB}$ | $\Delta G_{SWS}$ |
|---|---|---|---|---|---|---|---|---|
| Alginate | 35.7±1.8 | 1.1±0.4 | 3.8±0.6 | 4.0±0.7 | 39.7±1.4 | -3.4±0.5 | -58.0±2.2 | -61.4±1.6 |

[a] Values are given as average ± standard deviation (n=4)

According to the Eqs. (1-4), besides all the constant in the equations, the zeta potential of membrane and alginate, and the radius of alginate should be determined first to calculate various interfacial energy components versus separation distance between alginate and different membranes. Zeta potential and mean radius of alginate were determined by dynamic light scattering (DLS) with a Malvern Zetasizer, NANO ZS (Malvern Instruments Limited, UK), using a He-Ne laser (wavelength of 633 nm) and a detector angle of 173°. Zeta potential of the membrane surface was determined by a streaming potential analyzer (EKA 1.00, Anton-Paar, Swiss) following the procedure described by Childress and Elimelech.[4] The zeta potential measurement results are given in Table S4, and the mean radius of alginate was 218.1±12.3 nm. Zeta potential of membranes and alginate and the radius of alginate was substitute into Eqs. (1-4) to draw the interfacial energy versus separation distance curve between alginate and different membranes.

Table S4 The zeta potential of membranes and alginate[a]

| | T-0 | T-0.02 | T-0.05 | T-0.1 | T-0.5 | Alginate[b] |
|---|---|---|---|---|---|---|
| Zeta potential (mV) | -13.5±3.2 | -26.2±3.7 | -35.1±2.3 | -23.7±2.9 | -19.1±3.6 | -41.6±1.3 |

[a] 5 measurements were conducted for each sample

[b] ionic strength=10 mM, pH=6.5

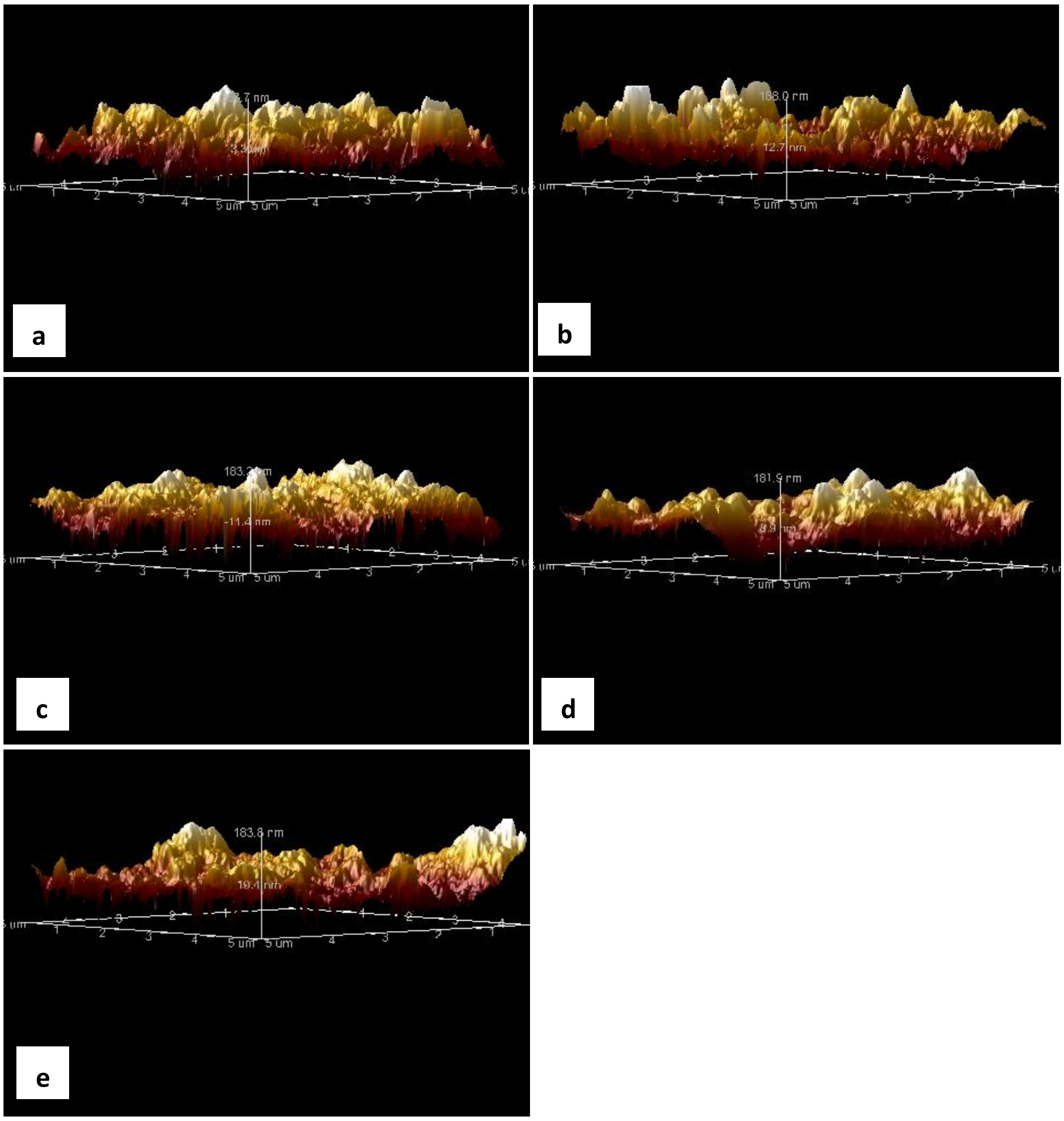


Fig. S1 AFM images and roughness of the membranes. (a~e) are AFM images of T-0~T-0.5 membrane, respectively.

References

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