

Supporting Information

Characteristics of Self-Assembled Ultra-thin Nafion Films

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This supporting information details Nafion-water dispersion preparation procedure, the ellipsometry fitting results, comparative ellipsometry raw data, and refractive index data of both type of films obtained from IPA diluted dispersion and water dispersion of Nafion. It also presents AFM images of the film prepared from Nafion-water dispersion.

Ellipsometry fitting results of the ultra-thin Nafion film from IPA diluted Nafion dispersion

Table 1: Summarized data for Nafion film prepared from IPA diluted Nafion dispersion.

Nafion Concentration	Nafion Layer thickness (nm)	Refractive Index at 550 nm	Non-Uniformity (%)
01 wt%	4.0	1.19	3.94
0.25 wt%	10.5	1.30	4.41
0.5 wt%	31.5	1.37	9.87
1.0 wt%	57.3	1.37	17.07
1.5 wt%	74.7	1.37	9.80
2.0 wt%	110.1	1.37	13.08
3.0 wt %	160.1	1.37	8.80
5.0 wt%	307.7	1.39	24.25

Preparation of ultra-thin films from Nafion-water dispersion

5 wt% Nafion stock dispersion in water was prepared by evaporating alcohol at 90 °C from 5 wt% Nafion dispersion (Nafion: water: alcohol; 5:20:75) as similar procedure has been described by Moore *et al.*¹ and Jiang *et al.*² for switching solvent in Nafion dispersion. It was considered that most of the alcohol was removed by 4 times repeated evaporation up to half of water weight of the dispersion (equivalent to 90% reduction in weight) and adjusting the total weight by adding water. Assuming equal rate of evaporation of water and alcohol, a conservative estimate of alcohol content in the final 5 wt% dispersion in water-based media is 0.0006 wt%. Significantly lower alcohol content is expected because alcohol is more volatile than water and more alcohol would be lost during evaporation. Different concentration of Nafion in water was prepared by adding Millipore water to the 5 wt% stock dispersion. The diluted dispersions were equilibration at least 24 hrs. Pre-cleaned substrates were immersed into the diluted dispersions for 12 hrs, took out and dried by N₂ gas blow.

Ellipsometry fitting results of the ultra-thin Nafion film from Nafion-water dispersion

Table 2: Summarized data for Nafion film prepared from Nafion -water dispersion.

Nafion Concentration (wt%)	Film thickness (nm)	Refractive Index At 550nm	Non-Uniformity (%)	Contact angle (°)	Roughness (nm)
0.25 wt%	11.6	1.32	1.68	<5	
0.5 wt%	27.5	1.36	4.90	<5	0.40
1 wt%	57.4	1.37	7.02	<5	0.38
3 wt %	172.9	1.37	14.24	105.7	0.43
5 wt%	312.7	1.38	19.21	105.6	0.44

Table 2 show that thicknesses & optical parameters and surface properties like surface wettability and roughness of the films obtained from self-assembly of Nafion-water dispersion at different Nafion concentrations. The characteristic film thickness and refractive index measured by Ellipsometry were very similar to the films obtained from Nafion dispersion in water/IPA mixture (Table-1). Similar film nano-structure/feature in between films obtained from two different dispersions might be supportive by the similar spectral response in ellipsometry spectra as presented in the fig.1. Water mediated films were also classified into two distinct categories hydrophilic and hydrophobic as same as water/IPA mediated films. Film morphologies and section analysis have been shown in the fig. 3 & 4 below.

Comparative ellipsometry raw data

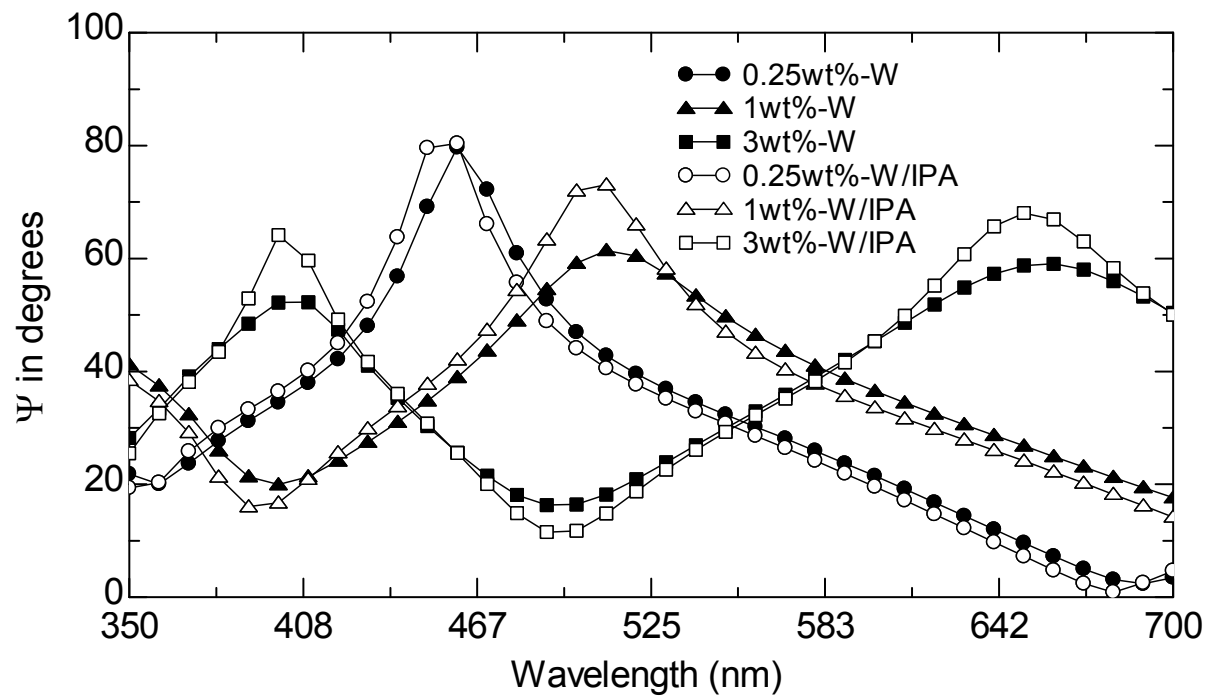


Fig.1: Comparative raw data of ψ spectra obtained from variable angle spectroscopic ellipsometry of three different corresponding films at 75° incident angle.

Comparative refractive indexes

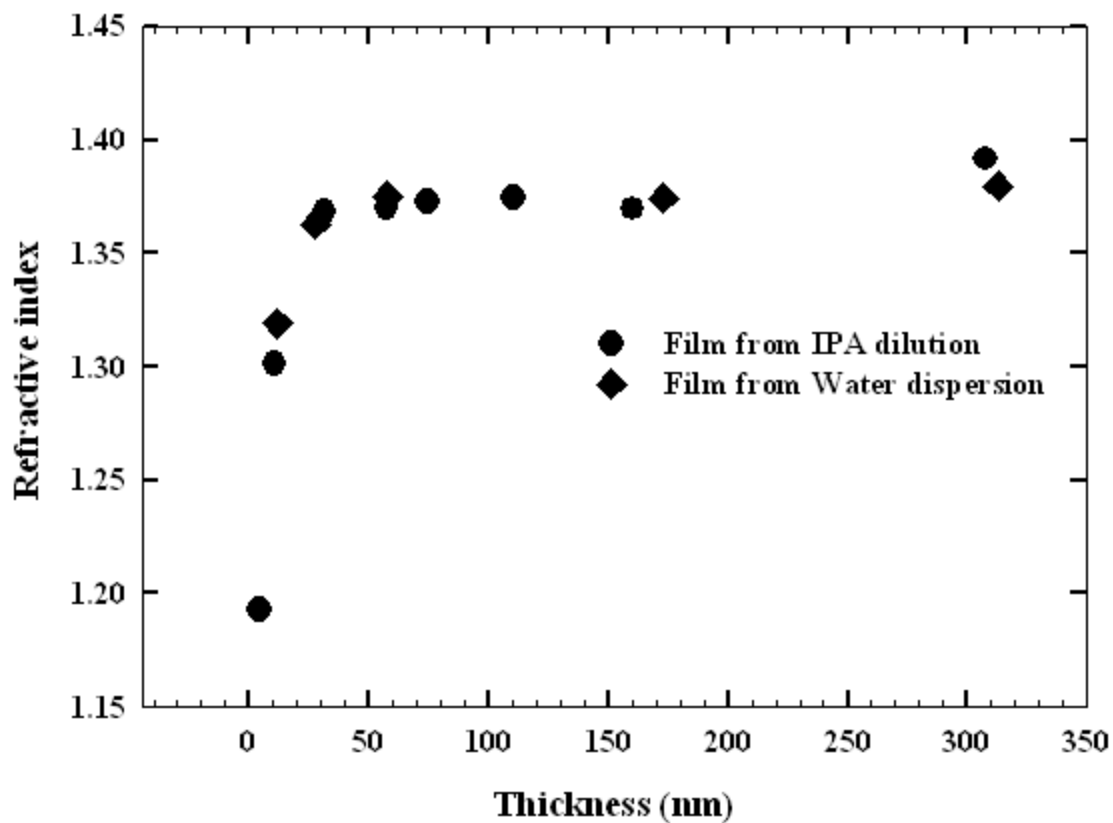


Fig.2: Refractive index of the films prepared from IPA diluted Nafion dispersion and Nafion-water dispersion in terms of thicknesses.

It was found that 4 and 10 nm film has lower RI whereas RI was almost constant from the film thickness 30 to 300 nm generated from IPA dilution dispersion. Interestingly, comparable RI was found from the films obtained from Nafion-water dispersion

AFM image of the films from Nafion-water dispersion

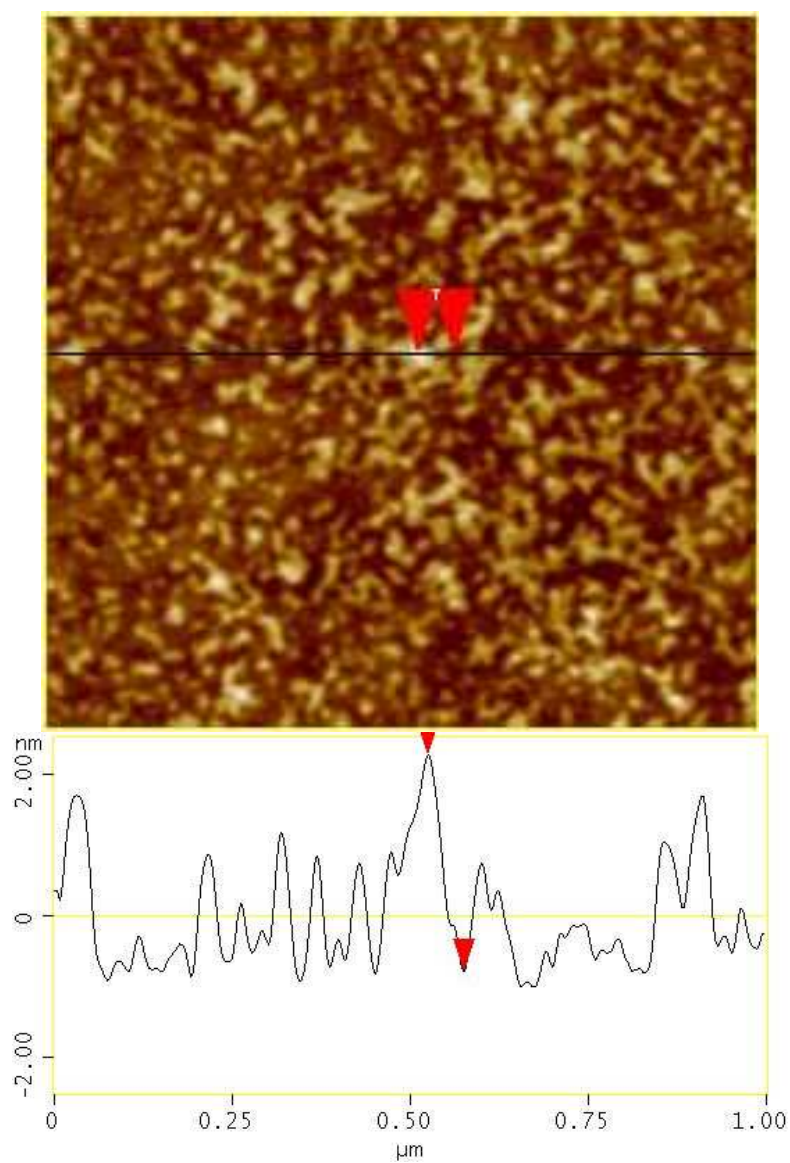


Fig. 3: Morphology and section analysis of corresponding self-assembled ultra-thin Nafion film of 0.1 wt% Nafion-water dispersion.

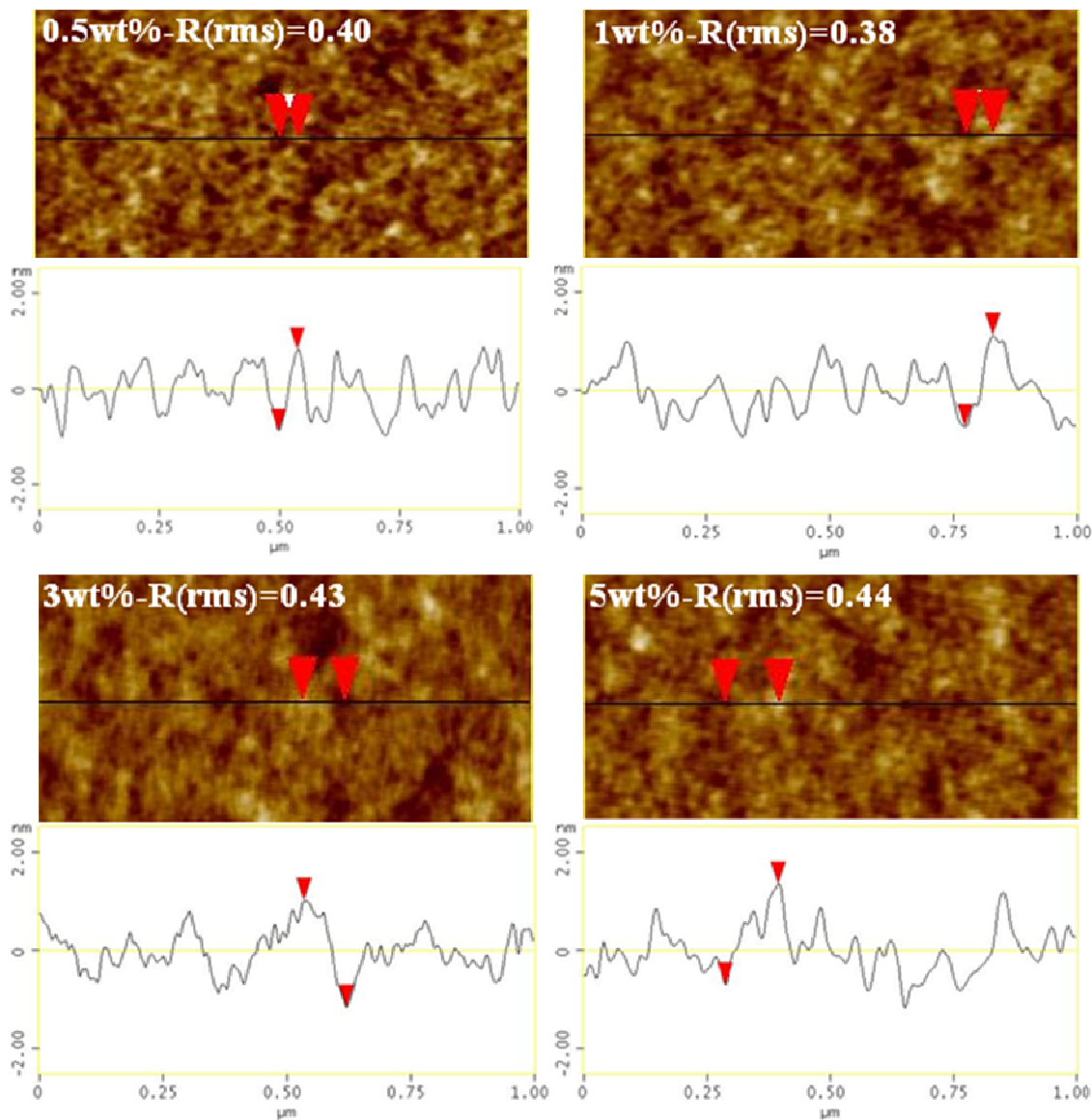


Fig.4: Morphologies and section analysis of self-assembled ultra-thin Nafion film prepared from different Nafion concentration in water.

Fig. 3 shows morphology and section analysis of 0.1 wt% film obtained from Nafion-water dispersion. Nafion has been scattered deposited where a significant part of substrate is completely uncovered. Section analysis shows that feature height varied from 2.5 to 3.5 nm

However, the corresponding film of Nafion-water dispersion concentration 0.25 wt% to 5 wt% have been presented in the fig.4 which shows continuous film with comparable corrugation with the film obtained from IPA diluted Nafion dispersion.

References

1. Moore, R. B., 111; Martin, C. R., *Macromolecules*, 1988, 21, 1334-1339
2. Jiang, S.; Xia, K-Q; Xu, G. Effect of Additives on Self-Assembling Behavior of Nafion in Aqueous Media, *Macromolecules* 2001, 34, 7783-7788