

Supporting Information for:

Surface Properties of Poly (vinyl alcohol) Films
Dominated by Spontaneous Adsorption of Ethanol
and Governed by Hydrogen Bonding

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Section 1: Determination of degree of hydrolysis of PVAs by ^1H NMR spectroscopy

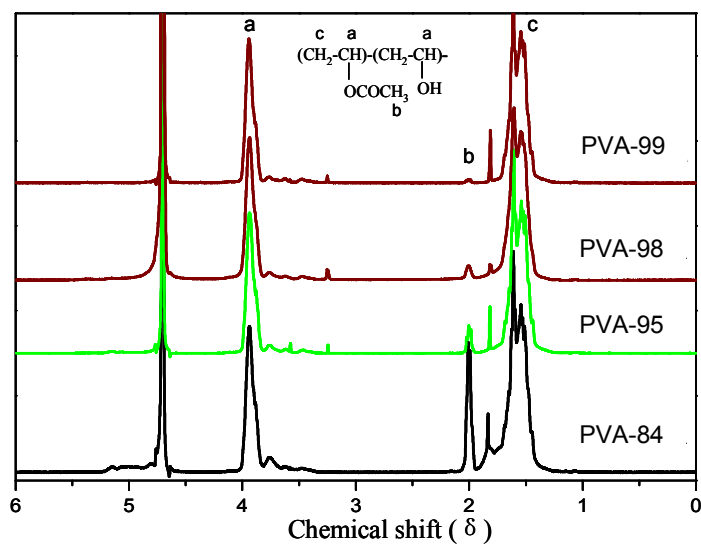


Figure S1. ^1H NMR spectra of PVAs with different hydrolysis degrees

The hydrolysis degrees were calculated from the ^1H NMR spectra of PVA/ D_2O solution, as shown in Figure S1. The peaks at 2.0 ppm and 3.9 ppm are from the CH_3 groups of VAc units and CH groups in the backbone, respectively. The hydrolysis degree can thus be estimated from the ratio of the integral peak areas.

Section 2: Surface roughness analysis by AFM for PVAs before and after immersion in ethanol

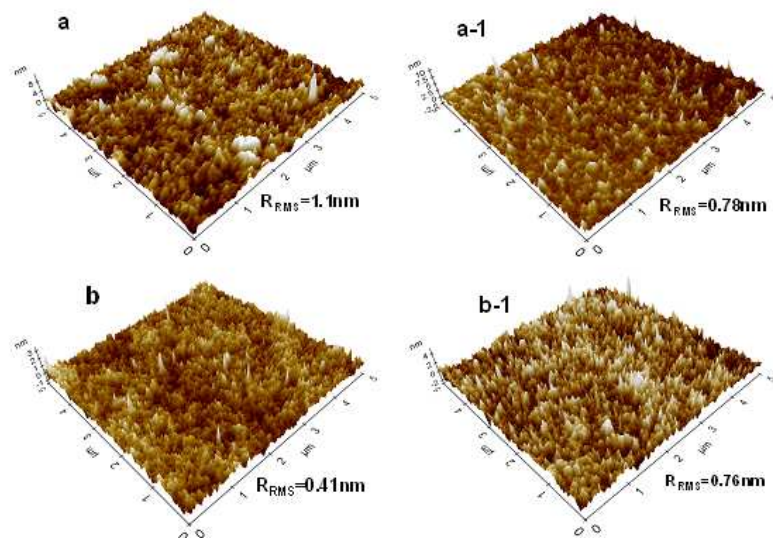


Figure S2. AFM images of PVA-99 (a) and PVA-84 (b) before (a, b) and after (a-1, b-1) immersion in ethanol for 30 min.

As is known, the surface roughness can substantially affect the measured contact angle¹. We thus investigated the change of the PVA surface topography after immersion in ethanol. Figure S2 shows the AFM topographic images of PVA-99 and PVA-84 before and after immersion in ethanol for 30 min (after 30 min, the measured contact angles leveled off). It can be seen that the immersion treatment has little influence on the surface roughness. For PVA-99, the RMS roughness changed from 1.1 nm to 0.8 nm. For PVA-84, the RMS roughness changed from 0.4 nm to 0.8 nm. The surface roughness change was far less than 100 nm, which is believed to be the critical value to of roughness that affects the measured contact angles¹. The very

smooth PVA surface after immersion in ethanol also indicates that the PVA films with various hydrolysis degrees are not swollen by ethanol in the time scale of immersion treatment, even if the immersion temperature is up to 60°C. Therefore, the measured contact angles were not affected by the surface roughness but caused by surface molecular structural changes like adsorption or/and restructuring.

Section 3: ATR-FTIR spectra of PVA-99 film before and after immersion in ethanol

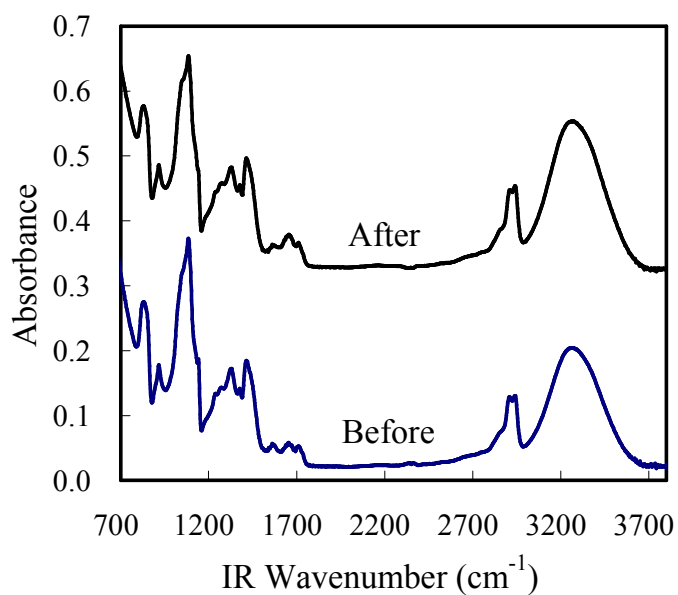


Figure S 3. ATR-FTIR spectra of PVA-99 films before and after immersion in ethanol for 30 min.

References

- (1) Busschera, H. J.; van Pelta, A. W. J.; de Boera, P.; de Jonga, H. P.; Arends, J. *Colloids and Surfaces* **1984**, *9*, 319-331.