## **Supplemental Information**

## Surface Defects in Polyelectrolyte Multilayers: Effects of Drying and Deposition Cycles

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Fig. S1 shows the AFM images of the surfaces of  $PEM_4^{dry}$  and  $PEM_8^{dry}$ .



Fig. S1. AFM images (5×5  $\mu$ m) of PEM<sub>4</sub><sup>dry</sup> (left ) and PEM<sub>8</sub><sup>dry</sup> (right), respectively

Fig. S2 shows the TEM image of a  $PEM_{4.5}^{dry}$  film, with PSS as the (negatively charged) cap layer, and it can be seen that AuNPs only scarcely adsorbed to the PEM surface, in sharp contrast with the dense coverage of AuNPs on the surface of the PEM with PDDA as the cap layer (PEM<sub>4</sub> and PEM<sub>8</sub>). This is direct evidence that the adsorption between the AuNPs and PDDA is through electrostatic interactions.



Fig. S2. TEM images of  $PEM_{4.5}^{dry}$  coordinated with AuNPs. The scale bars are 100

## nm.

XPS was used to further analyze the contents of PSS and PDDA in PEM<sub>4</sub>. The N/S ratios were 0.44 and 0.48 for  $PEM_4^{wet}$  and  $PEM_4^{dry}$  respectively.

For the PEMs assembled in the presence of 0.1 M NaCl, PSS contents were compared by UV-vis spectroscopy, and the spectra are shown in Fig. S3. It can be seen that more PSS is present in  $PEM_4^{dry}$  than  $PEM_4^{wet}$ , and based on the peak intensities the ratio of PSS in  $PEM_4^{wet}$  vs  $PEM_4^{dry}$  is 1:1.16. Furthermore, XPS data show that the N/S ratios are 0.53 and 0.87 for the  $PEM_4^{wet}$  and  $PEM_4^{dry}$ , respectively, again indicating that drying leads to greater amounts of PDDA deposited in  $PEM_4$ compared with the one without drying.



**Fig. S3.** UV-vis spectra of  $PEM_4^{wet}$  and  $PEM_4^{dry}$  assembled in the presence of 0.1M NaCl. The films were deposited on quartz slides.

Also included is a video clip showing a water droplet advancing on the surface of  $PEM_8^{dry}$ . When water is continuously added to the droplet, a distinct "stick-slip" motion of the water contact line can be clearly observed. This behavior is resulted from the pinning-depinning of the moving contact line of the water droplet at hydrophilic defects on the PEM surface.