Supporting Information

Facile formation of nanoparticle patterns by water induced flow of polymer thin film

Xiao Gong*

College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

** Email: gongxiaopattern@gmail.com*

To measure the film thickness, part of the films was scratched off by a thin needle of syringe. Then the height difference between the exposed silicon substrate and the multilayers was measured by SFM. The thickness of the PEI(PSSMA/PDADMAC)$_7$ multilayers was measured as about 40 nm by SFM (Fig. S1), which is consistent with the ellipsometry result.

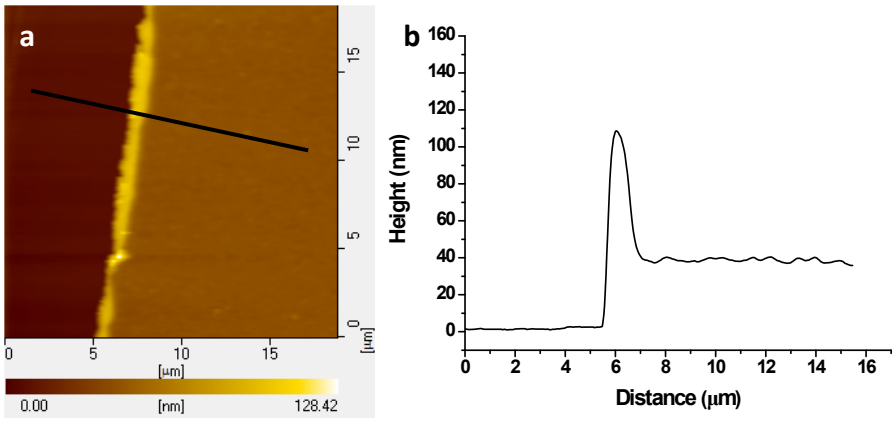

Fig. S1 (a) SFM image of PEI(PSSMA/PDADMAC)$_7$ multilayers. One part of the multilayers was scratched off to measure the film thickness (b) its corresponding line profile.

In order to explore the flow of the film, part of the multilayers was scratched off with a thin needle of syringe along the perpendicular direction of the linear patterns (Fig. S2). As shown in Fig. S2, The total heights of the patterns (the height difference between non-contact areas of the multilayers and silicon substrate) are about 75-80

nm (the black line), which are much larger than the pristine thickness of the PEI(PSSMA/PDADMAC)$_7$ multilayers (~ 40 nm, Fig. S1). While the thickness of the multilayers in the contact areas, namely the thickness of the polyelectrolyte multilayers that remain after the polyelectrolyte multilayers moved, is about 15-20 nm (the height difference between contact areas of the multilayers and silicon substrate) represented by the red line, which is much smaller than the pristine thickness of the multilayers. Thus, the decreased height of the multilayers in the contact areas is around 20 nm, while the increased height of the multilayers in the non-contact areas is around 40 nm. This result clearly reveals the wet PDMS stamp causes the polyelectrolyte multilayers to move from contact areas to non-contact areas, and patterns are formed by the flow of the multilayers instead of swelling because film thickness in contact areas is much smaller than original film thickness. As we know the water molecules may be function as the plasticizer to soften the films. Consequently, the films in the contact regions of the stamp are pushed to the non-contact regions under the capillary force. The patterns are thus formed by the films flowed from the two edges of the contact regions. At the same time, a more loosely patterned structure is assumed to produce in the non-contact regions during the flow of polyelectrolyte multilayer film since the increased thickness is much larger than decreased thickness.

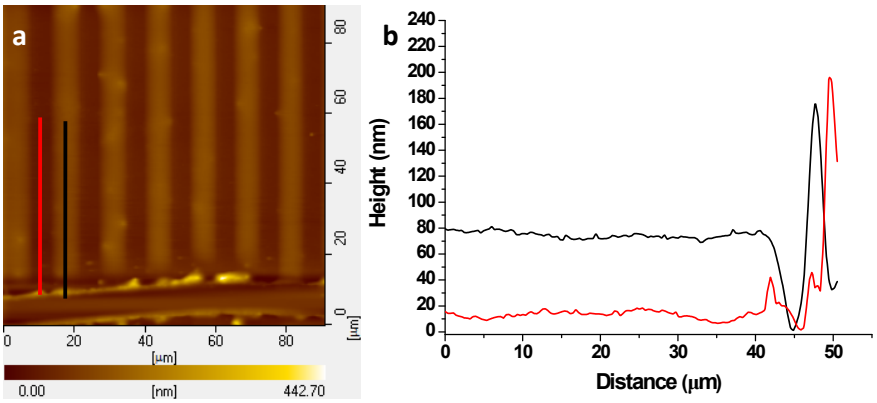

Fig. S2 SFM image of water induced patterns of PEI(PSSMA/PDADMAC)$_7$ multilayers (a). (b) cross-sectional line profiles recorded in the positions shown in (a).

In addition to PSSMA/PDADMAC pairs, this process of water induced patterned

structures could also be applied to other pairs such as PSS/PDADMAC, and PAA/PDADMAC. As shown in Fig. S3, pattern structure can be clear seen on the surface of PSS/PDADMAC and PAA/PDADMAC films, respectively.

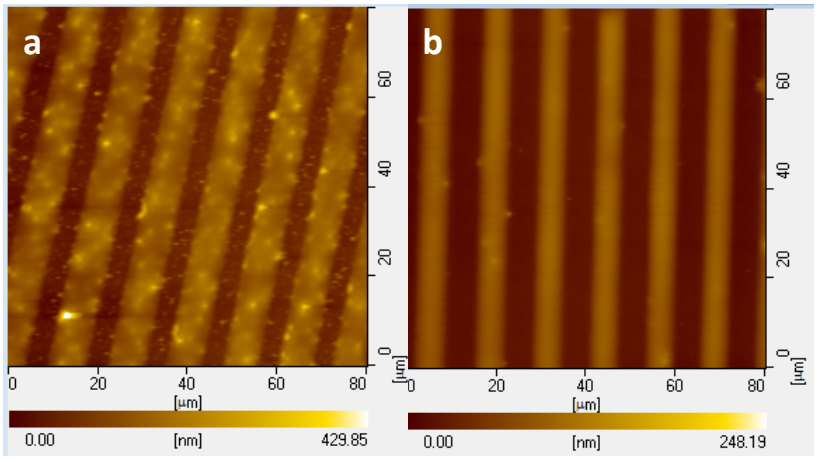

Fig. S3 SFM image of water induced patterns of PEI(PSS/PDADMAC)$_7$ multilayers (a), and PEI(PAA/PDADMAC)$_7$ multilayers (b).

In order to explore that forming arrays of silica particles on the multilayers are not limited to the certain size of silica and the positive charged outermost layer. The 200 nm silica nanopartciles were applied to the pattern arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers when PSSMA was the outermost layer which is negatively charged. Interestingly, we have also successfully obtained nanoparticle arrays on the polyelectrolyte multilayers using this simple method (Fig. S4). We assume the strong capillary force exists between the PDMS stamp and the multilayers causing the polyelectrolyte multilayers and nanoparticles to move from contact regions to non-contact regions. Fig. S4a shows bright field microscope image of 200 nm SiO_2 nanoparticle arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers, and Fig. S4b shows dark field microscope image of SiO_2 nanoparticle arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers. Both images clearly showed SiO_2 nanoparticles were well patterned arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers. Fig. S4c shows the SFM image of SiO_2 nanoparticle patterned arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers.

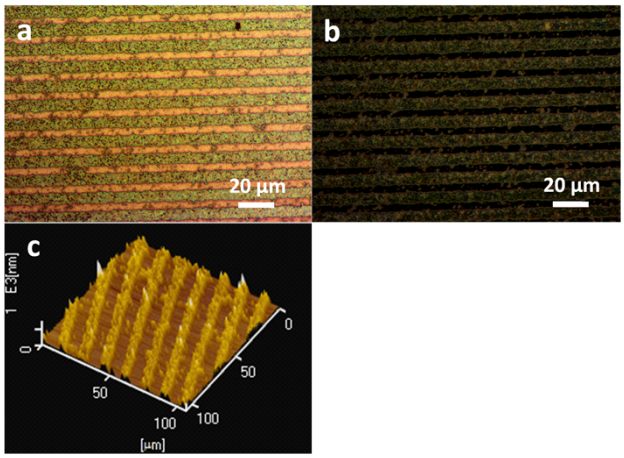

Fig. S4 (a) Bright field microscope image of SiO_2 nanoparticle arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers, and (b) Dark field microscope image of SiO_2 nanoparticle arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers. (c) SFM images of SiO_2 nanoparticle arrays on the PEI(PSSMA/PDADMAC)$_6$PSSMA multilayers.