Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Directed patterning of the self-assembled silk-elastin-like nanofibers using nanomechanical stimulus

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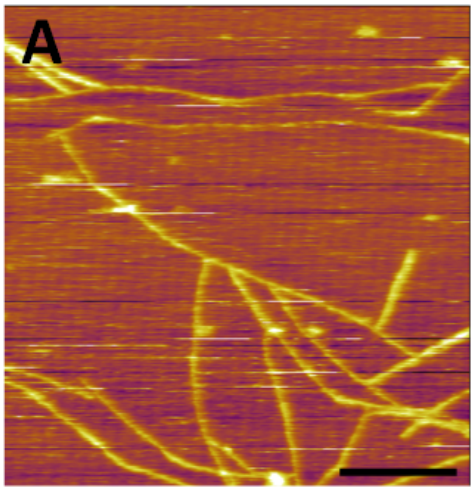
1. Materials and Methods

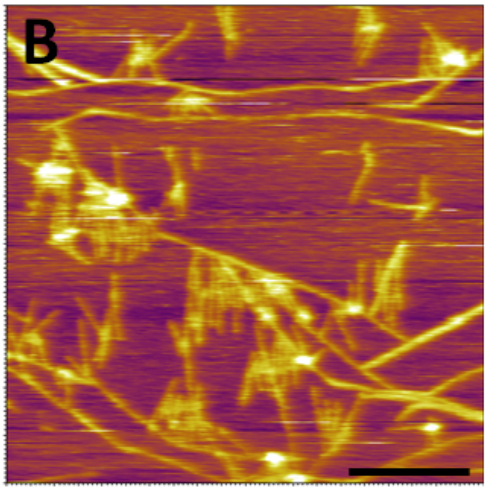
The repeating monomer of SELP-815K consists of 8 silk-like units (GAGAGS), 15 elastin-like units (GVGVP), and 1 elastin unit modified by the substitution of valine for lysine (GKGVP). The complete polymer contains 6 tandem repeats of the monomer sequence. The full amino acid sequence of SELP-815K including the non-repeating head and tail sequences is as follows: MDPVVLQRRDWENPGVTQLNRLAAHPPFASDPM[GAGS(GAGAGS (GVGVP GKGVP(GVGVP (GAGAGS GAGA MDPGRYQDLRSHHHHHH

A silicon nitride tip (MLCT, Bruker, Camarillo, CA) with a spring constant of 0.03 N/m was used to image the nucleation areas in a tapping mode. The free amplitude was set to 400 mV and the setpoint varied between 280-380 mV. The tapping forces based upon the ratios of setpoint/free amplitude ranged from 2.3 nN to 6.32 nN.14 The scan speeds were varied f rom 5 to 15 µm/sec and the number of scan lines were varied from 64 to 1024 lines in 2 µm x 2 µm scanned area. The nucleation area and nanofiber coverage was quantified using ImageJ software.

2. The effect of the mechanical stimulus on the nanofiber growth in the presence of soluble SELP protein

We examined the effect of nanomechanical stimulus in the presence of SELP proteins in solution (without washing after incubation). When we apply tapping force using AFM, nanofibers still grew due to the nanomechanical stimulus. (Fig. S1(B)) The average initial fiber coverage in SELP solution was 8.14 % (Fig. S1(A)) and the increase in fiber coverage in the second scan was 3.54% (Fig. S1(B)). The increase in fiber coverage was not significantly





different from the fiber coverage increase of washed samples (in the absence of soluble SELP). This implies that as long as the surface is densely covered during incubation stage, the presence of the soluble SELP may not affect the growth behavior of SELP nanofibers considerably. This observation further suggests that the adsorption of SELP on the mica at a high density and the interactions between AFM tip and adsorbed SELP are playing a major role in nanomechanically assisted self- assembly of SELP.

Figure. 1S. (A) The first scanned AFM image in the presence of soluble SELP after incubation, (B) the second scanned AFM image of the same area in the presence of soluble SELP. The scale bar is 500 nm. (Tapping mode imaging conditions: scan size = 2 µm by 2 µm; scan speed = 7.5 µm/s; scan lines = 512; setpoint/free amplitude = 320/400 mV)

3. The stability of the nanofibers

Once the nanofibers were formed, the nanofiber structure is very stable and it maintained its structural features in PBS buffer as well as in distilled water. We have not observed the dissolution of protein nuclei and nanofibers in DI water even after weeks, which suggests that formation of nanofibers is an irreversible process under the conditions that we tested. SEM image of Fig. S2 shows that nanofibrous structures remained stable in air as well. However, we cannot rule out a possibility of dissolution of nanofibers when the solvent quality is changed.

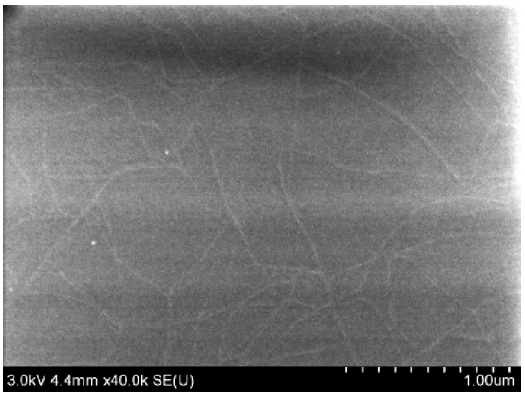


Fig. 2S. The SEM image of SELP nanofibers in air.

4. The evidence of tip-SELP interactions measured by AFM

We measured the interactions forces between SELP and silicon nitride tip using AFM. The following Fig. S3 shows 30 overlaid force curves measured in water at room temperature. The tip velocity was 2 µm/sec and the maximum contact force was 250 pN. The blue color dots shows force profile during tip approach and red color dots shows force profile during tip retraction. When tip approached SELP coated surface, the attractive force was observed. The average attractive force was 66.6 ± 9.4 pN at 8.1 nm from the surface. The attractive force was

relatively long range in water and electrostatic interactions between positively charged SELP and negatively changed silicon nitride tip are considered to be a major component of this attractive force. During tip retraction from the surface, adhesion force was observed and most of the curves showed stretching behaviors of polymeric molecules, indicating that SELP was attached to the tip and most of them are extended up to ~169.4 ± 34.57 nm. During tapping mode imaging, nN force is applied to SELP and these force profile provides direct evidence that AFM tip can pick up SELP molecules from the surface through attractive interactions between them.

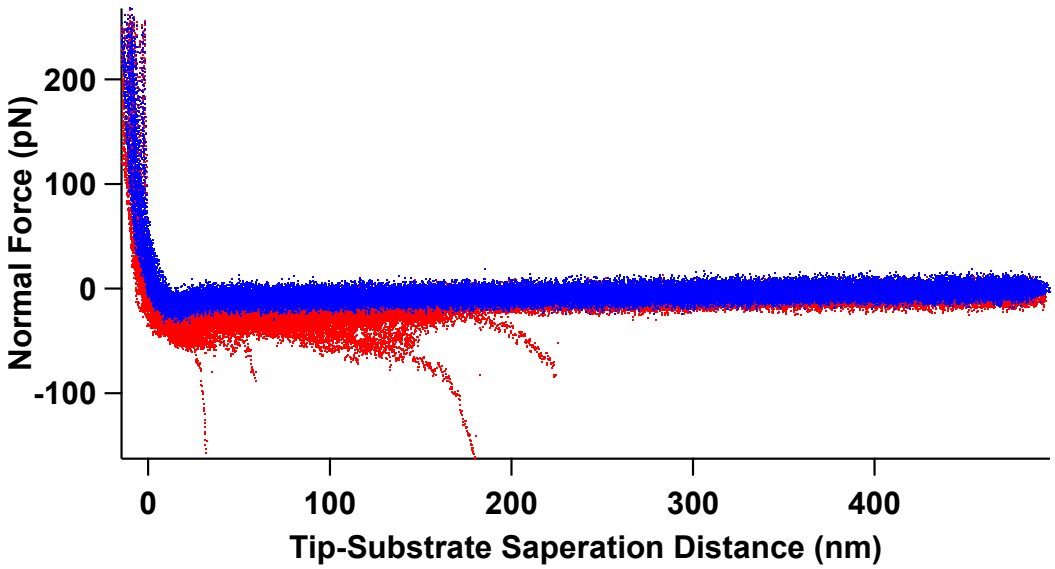


Fig. 3S. The force profiles measured between SELP coated mica substrate and silicon nitride AFM tip. 30 force profiles are overlaid. Blue dots were obtained during tip approach and red dots were collected during tip retraction.