

## Electronic Supplementary Information

### **Bio inspired stimuli-responsive multilayer film made of silk-titanates nanocomposite**

Elena Colusso<sup>a</sup>, Giovanni Perotto<sup>b</sup>, Yu Wang<sup>c</sup>, Marco Sturaro<sup>a</sup>, Fiorenzo Omenetto<sup>c</sup>, Alessandro Martucci<sup>a\*</sup>

<sup>a</sup> Università di Padova, Dipartimento di Ingegneria Industriale, Via Marzolo, 9, 35131 Padova, Italy

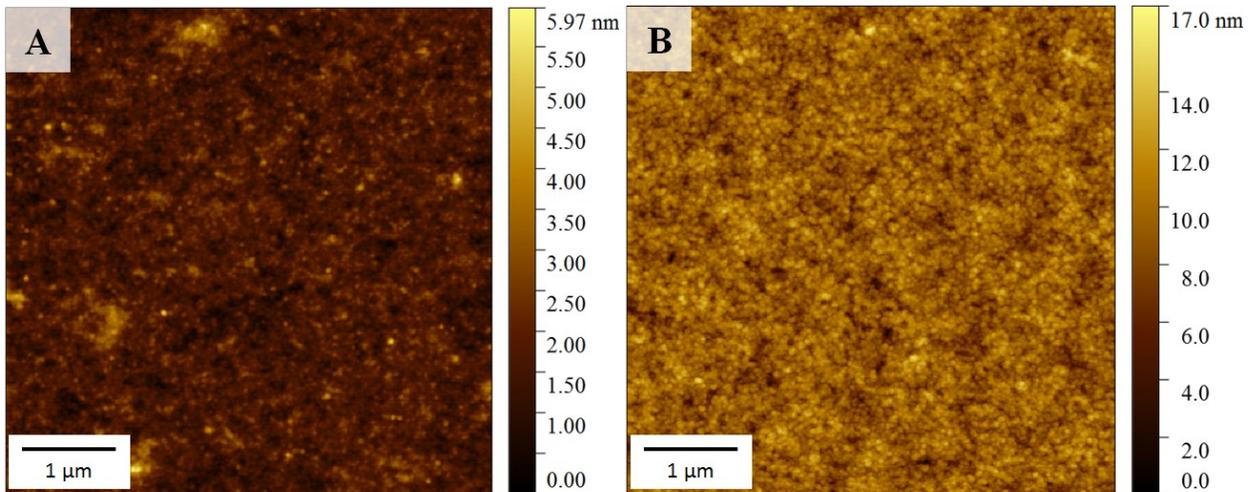
<sup>b</sup> Smart Materials, Istituto Italiano di Tecnologia (IIT), via Morego 30, 16163 Genova, Italy

<sup>c</sup> Department of Biomedical Engineering and Department of Physics, Tufts University, 4 Colby St., Medford, MA 02155, USA

**Table S1:** Effect of methanol annealing on the thickness and the refractive index of the film (at  $\lambda=500$  nm) deposited on silicon substrate. The values reported are obtained from spectroscopic ellipsometry by fitting the experimental data with a Cauchy dispersion equation. Each value is an average over 5 samples.

	<b>Rsilk</b>			<b>HRIsilk</b>		
	<i>As deposited</i>	<i>MeOH annealing</i>	<i>Variation (%)</i>	<i>As deposited</i>	<i>MeOH annealing</i>	<i>Variation (%)</i>
<b>Thickness (nm)</b>	82 $\pm$ 2	80 $\pm$ 2	-2.5	93 $\pm$ 2	42 $\pm$ 5	-55
<b>Refractive index</b>	1.54	1.56	1.3	1.62	1.82	12.3

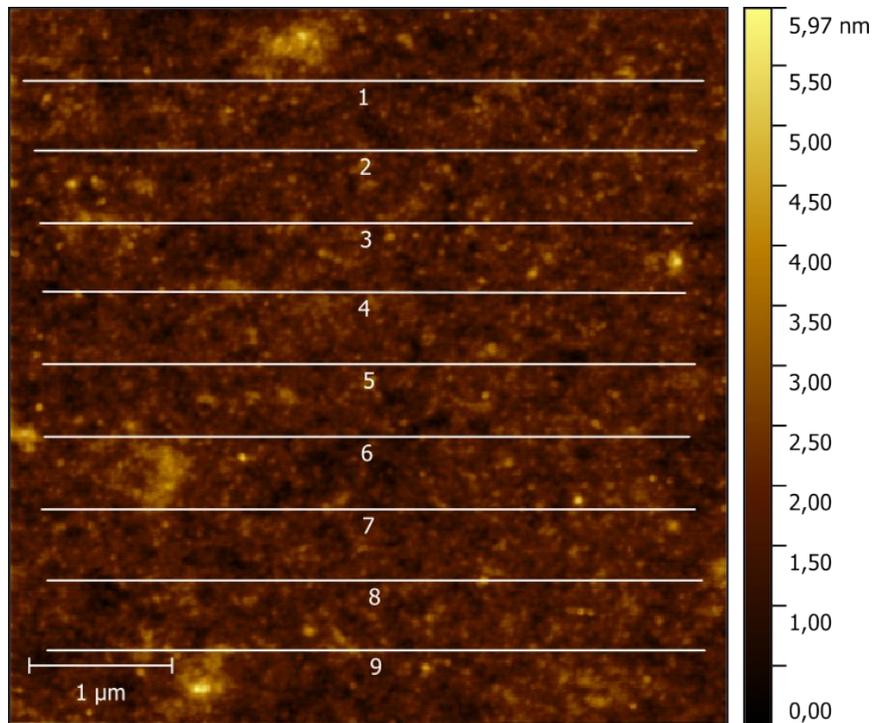
**Figure S1:** AFM micrograph of Rsilk film (A) and HRIsilk film (B) deposited on Si wafer after methanol treatment.



**Table S2:** Roughness average (Ra) and root-mean-square roughness (rms) of R silk film. The values reported are calculated on profile extracted from a 5x5 $\mu$ m AFM images (Figure S2).

Profile	Ra [nm]	rms [nm]
1	0.381	0.488
2	0.344	0.435
3	0.447	0.549
4	0.395	0.486
5	0.316	0.396
6	0.399	0.495
7	0.415	0.515
8	0.297	0.375
9	0.443	0.565

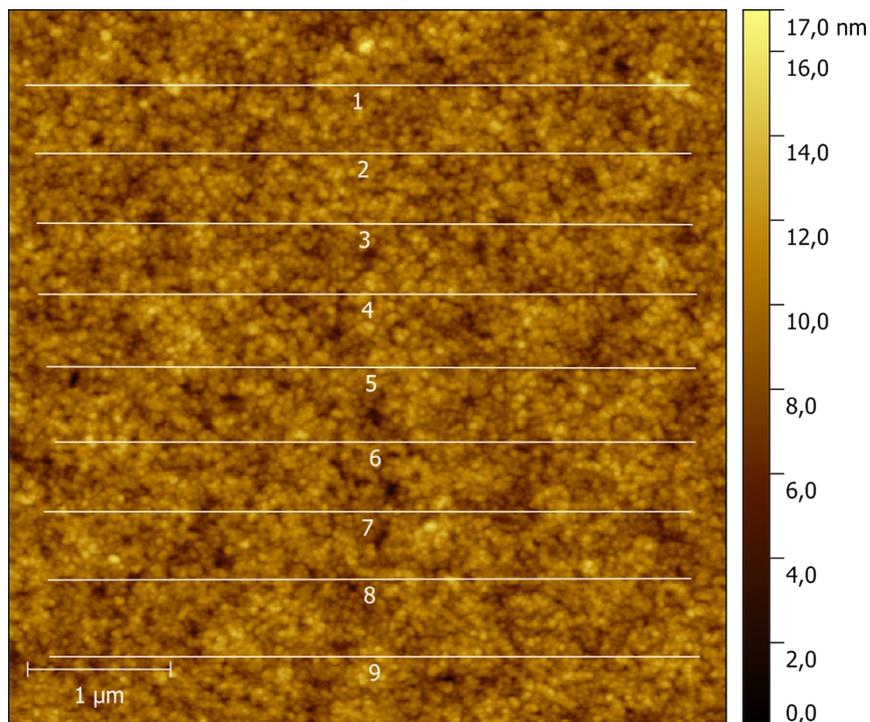
**Figure S2:** AFM image of Rilk film with the profiles corresponded to the roughness values reported in Table S2.



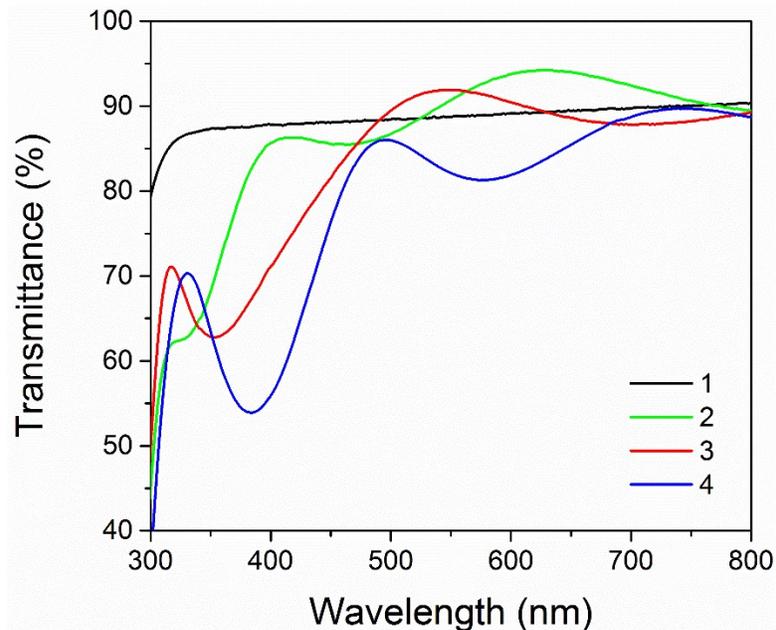
**Table S3:** Roughness average (Ra) and root-mean-square roughness (rms) of HRIsilk film. The values reported are calculated on profile extracted from a 5x5 $\mu\text{m}$  AFM images (Figure S3).

Profile	Ra [nm]	rms [nm]
1	1.501	1.891
2	1.012	1.319
3	1.179	1.505
4	1.075	1.370
5	1.156	1.443
6	1.222	1.558
7	1.141	1.462
8	1.079	1.354
9	1.215	1.535

**Figure S3:** AFM image of HRI silk film with the profiles corresponded to the roughness values reported in Table S3.



**Figure S4:** Transmittance spectra of multilayers structure for 1, 2, 3 and 4 couples of Rsilk and HRIsilk layers.



**Table S4:** Thickness and refractive index of Rsilk and HRIsilk films of the best fitting of experimental transmittance spectrum of the multilayer, obtained through simulation.

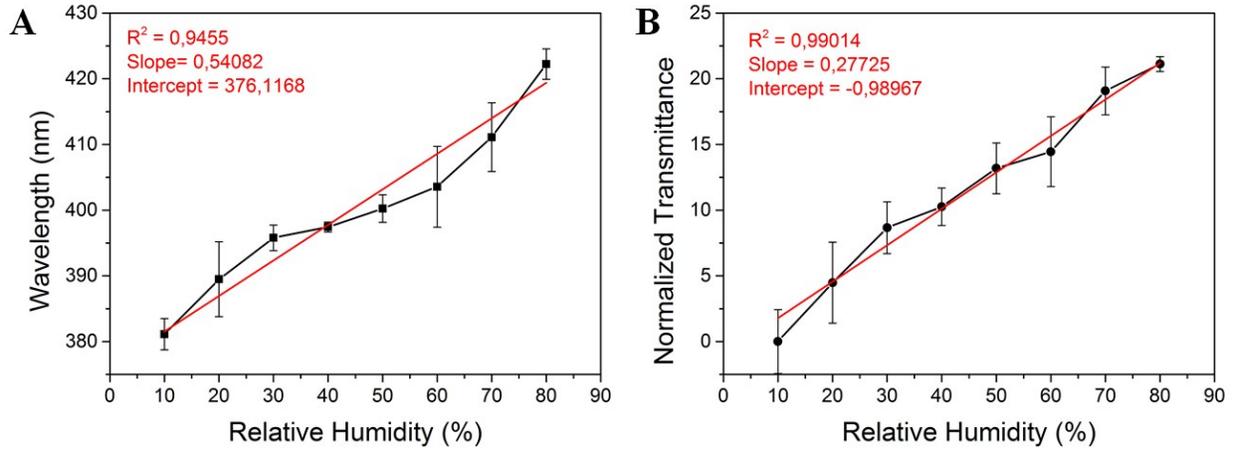
	<b>Rsilk</b>	<b>HRIsilk</b>
<b>Thickness (nm)</b>	80	39
<b>Refractive index @500nm</b>	1.56	1.80

**Table S5:** Thickness and refractive index of Rsilk and HRIsilk films of the best fitting of experimental data for different humidity conditions: 10% RH and 80% RH.

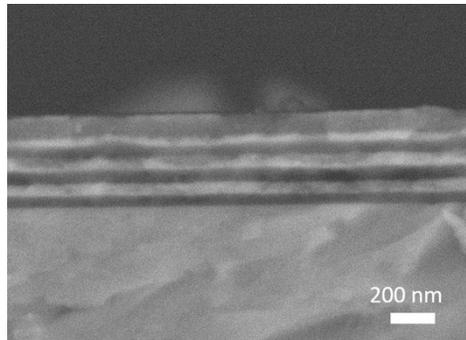
	<b>Rsilk</b>			<b>HRIsilk</b>		
	<i>10%RH</i>	<i>80%RH</i>	<i>Difference</i> (%)	<i>10%RH</i>	<i>80%RH</i>	<i>Difference</i> (%)
<b>Thickness (nm)</b>	78	90	15	37	47	27
<b>Refractive index @500 nm</b>	1.58	1.52	-3.8	1.83	1.75	-4.5

For the modeling both the refractive index of the layers and the film thickness were fit as the humidity changed. We observed that the structure responded with a reduction of the thickness and a partial increase of refractive index of the layers due to the loss of water when RH decreased from 80% to 10%. This behavior induces a blue-shift of the interference peak and an increase of the reflectivity compared to standard condition. On the other hand, when RH is increased from 10% to 80%, water adsorption causes a swelling of the layers and a reduction of refractive index. The best fitting of experimental data obtained from simulations estimates that the increase of thickness is  $\square 15\%$  for Rsilk and  $\square 27\%$  for HRIsilk, while the decrease of refractive index is  $\square 2.5\%$  and  $\square 4.5\%$  for Rsilk and HRIsilk, respectively.

**Figure S5:** Plot of interference peak position and transmittance at 360 nm versus RH of the multilayer structure. Each point is an average of 5 measurements (error bars correspond to standard deviation). It is also reported the linear fit of the experimental points (red line) used to calculate the sensitivities reported in the main text.



**Figure S6:** Cross-section SEM image of the multilayers structure deposited on fused quartz after several cycles of humidity treatment.



**Table S6:** Hysteresis values calculated from the curves reported in Figure 4D, E and F.

<b>RH (%)</b>	<b>Hysteresis for Wavelength (%)</b>	<b>Hysteresis for Transmittance @ 360 nm (%)</b>	<b>Hysteresis for FWHM (%)</b>
<b>10</b>	0.14	0.98	0.48
<b>20</b>	0.83	2.58	0.78
<b>30</b>	1.04	3.41	0.93
<b>40</b>	0.18	0.90	0.43
<b>50</b>	0.58	2.78	1.24
<b>60</b>	0.79	-0.71	0.54
<b>70</b>	0.79	3.03	1.69

**Video S1**