Electronic Supplementary Information

Spontaneous wrinkle emergence in nascent eumelanin thin films.

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Methods

DHI thin film preparation

DHI thin films were prepared with a spin coater (Laurell, mod. WS-650MZ-23NPP/LITE); thin films were deposited on glass substrates and were obtained from solutions of DHI in methanol at different concentrations. After filtering the solution through a 0.2 μm nylon membrane, the following speed increments were used: 2000 rpm for 90 s; 800 rpm for 10 s and then 3000 rpm for 60 s; 2000 rpm for 60 s; and 3000 rpm for 90 s. In some cases thin films were also annealed at 70 °C for 30 min under nitrogen atmosphere.

Ammonia-Induced Solid State Polymerization

The oxidation of DHI thin films leading to melanin polymer has been achieved by exposure to an oxidizing atmosphere (e.g. oxygen atmosphere and ammonia vapors). In the general procedure, the appropriate film was incubated in the oxygen/ammonia atmosphere at controlled temperature (25 - 40 °C). The ammonia vapors were produced by equilibration of the atmosphere with ammonia solution (28% to 7% NH_3 in H_2O: fresh commercial ammonia solution (for analysis EMSURE®) with known concentration was which we used as is or after dilution in water) in a sealed camera at 1 atm pressure. Exposure times varied in the range 2 - 18 h.

Absorbance spectra

All absorbance spectra of eumelanin and DHI samples have been recorded with a commercial spectrophotometer (Perkin-Elmer, mod. Lambda 900). It is worth mentioning here that the contribution of the glass substrate sustaining sample is automatically subtracted from the acquired spectra by inserting a second identical substrate without any deposition into a reference arm of the spectrophotometer. Moreover, interference fringes occurring at wavelengths close to the film thickness have been averaged out with a software smoothing procedure.

Characterization of film surfaces

The thickness of the film right after deposition was determined by scratching the film down to the substrate with a razor blade and measuring the height of the resulting trench by means of a commercial profilometer (KLA Tencor, mod. P-6). However, when the surface roughness is of the order of hundreds of nanometers, thus comparable to the profilometer tip radius, the profilometer results are completely unreliable. In such cases it is necessary to employ an atomic force microscope (AFM), which also provides a wealth of additional information on both surface structure and composition.

AFM and Raman analysis were conducted with the integrated apparatus Alpha300 RS (WITec, Ulm, Germany). The system can be switched at will between AFM and confocal micro-Raman configurations, allowing a combined topographical and spectral characterization of a specified micro-region of the sample. The topography of the films was studied by operating the AFM in tapping mode using a cantilever with 75 kHz resonant frequency (and spring constant of k = 42 N/m). Image elaborations have been performed through the open source Gwyddion software.

For the micro-Raman analysis, a laser beam at $\lambda = 488$ nm at the power of P = 5mW was used as excitation light source. The beam was focused onto the sample surface by means of a 50× microscope objective (numerical aperture (NA) of 0.75) working in epi-illumination mode. The diffraction-limited focused spot in the objective focal plane had a full width at half-maximum (FWHM) of approximately 320 nm. The light backscattered from the sample was collected by the same objective, and sent to the spectrograph, equipped with a thermo-electric cooled back-illuminated CCD detector, through a confocal optical collection path. The reported Raman spectra are the result of the average of 25 single spectra acquired in different positions of the surface in order to take into account of eventual variations due to local inhomogeneity of the samples.

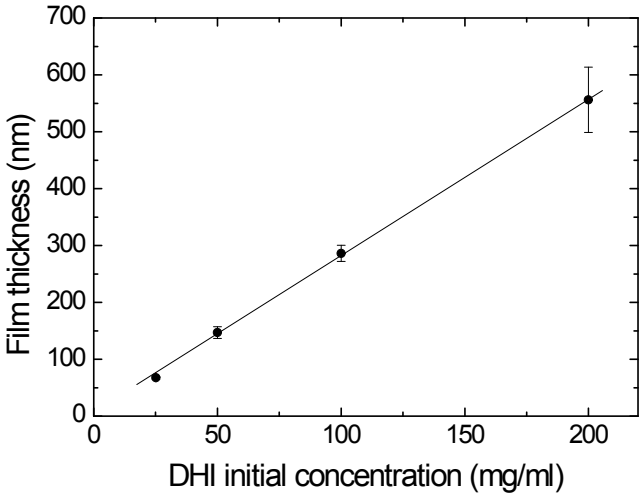

Figure S1. Thin film thickness vs. concentration of DHI in the starting solutions. The solid line is the linear fit to the data

Table S1. Concentration of the initial DHI solution and corresponding measured film thicknesses

DHI initial concentration (mg/ml)	25.0 ± 0.1	50.0 ± 0.1	100.0 ± 0.1	200.0 ± 0.1
Film thickness (nm)	57 ± 2	150 ± 10	290 ± 15	560 ± 50

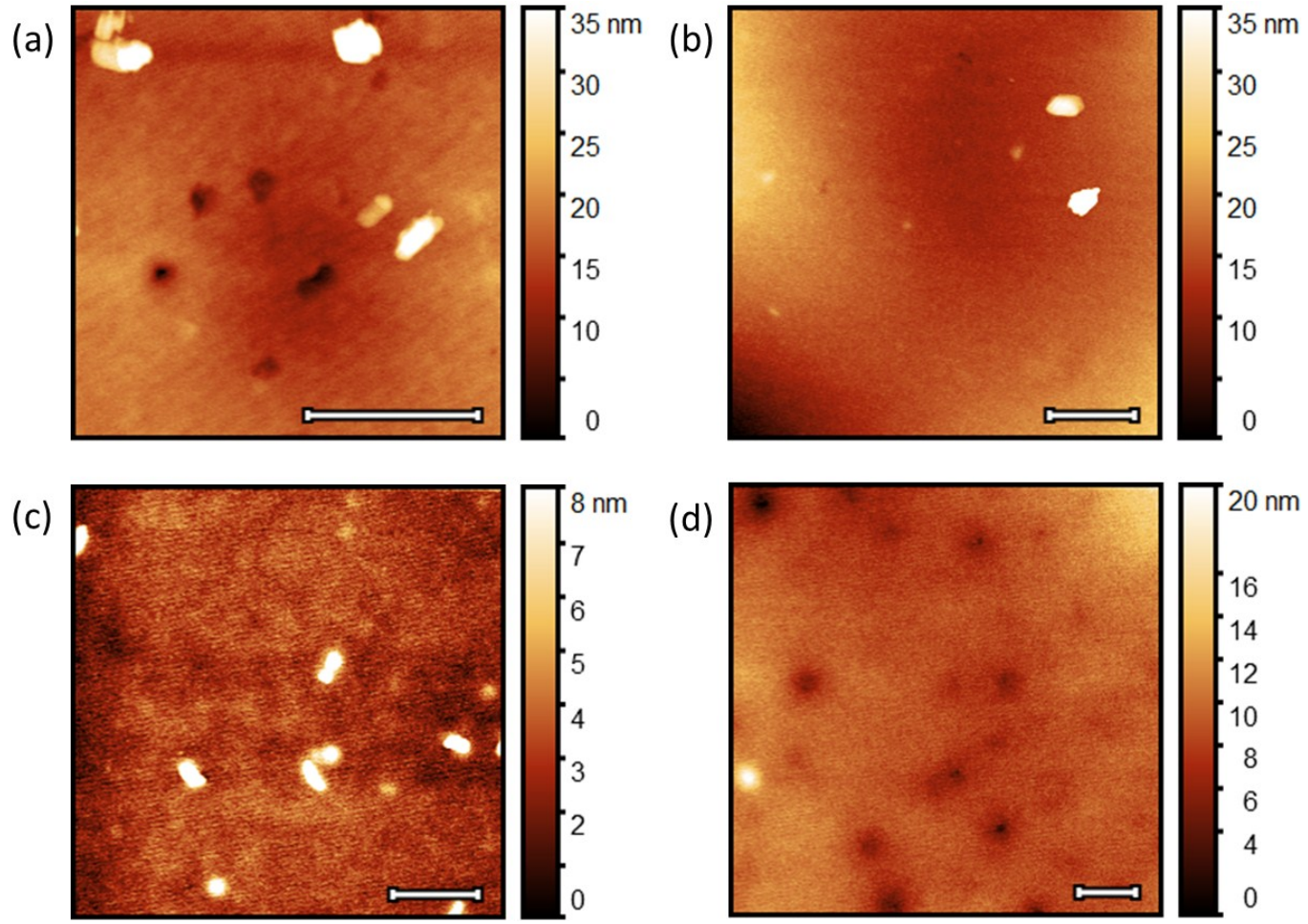

Figure S2. AFM images of spin-coated films at the time t_0 for the DHI concentration of: (a)25 mg/ml; (b) 50 mg/ml; (c) 100 mg/ml; 200 mg/ml. Scale bars 5 μm.

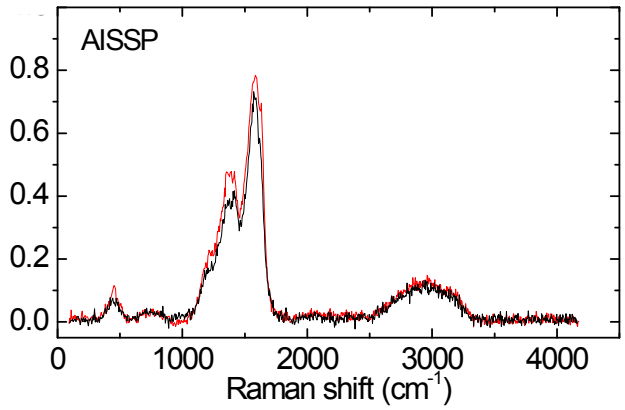

Figure S3. Raman spectra of 25 mg/ml (black curve) and 200 mg/ml (red curve) AISSP films.

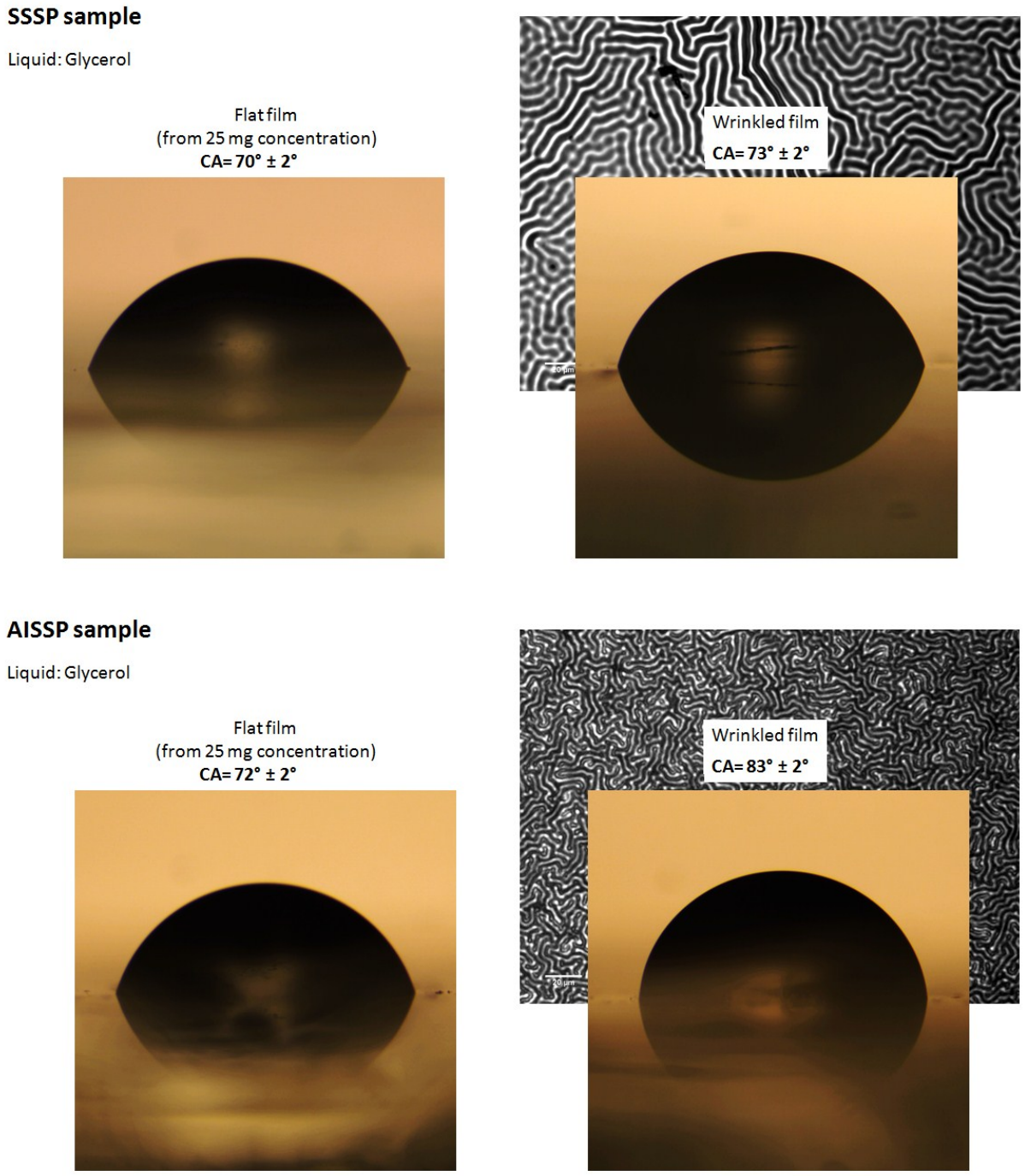

Figure S4. Measurement of static contact angle of a glycerol droplet on the SSSP and AISSP eumelanin film surfaces prepared from of 25 mg/ml (left) and 200 mg/ml (rigth) DHI solutions.