

Supplementary Information for:

Texture and Wettability of Metallic Lotus Leaves

C. Frankiewicz^a and D. Attinger^{a,*}

^a Iowa State University, Black Engineering Building, Ames, IA – 50011

* Corresponding author: attinger@iastate.edu

Influence of the reaction parameters (temperature, concentration, time) on the surface texture and wettability.

The temperature and concentration of the chemicals used for modifying the surface had a strong influence on the size and type of microstructure. Inspection of Surface E1 in Fig. S1 reveals that the lower the temperature, the higher the density of copper microstructures; and that the lower the concentration of FeCl_3 (Blue number, varied from 0.1g to 5g) the higher the density of copper microstructures.

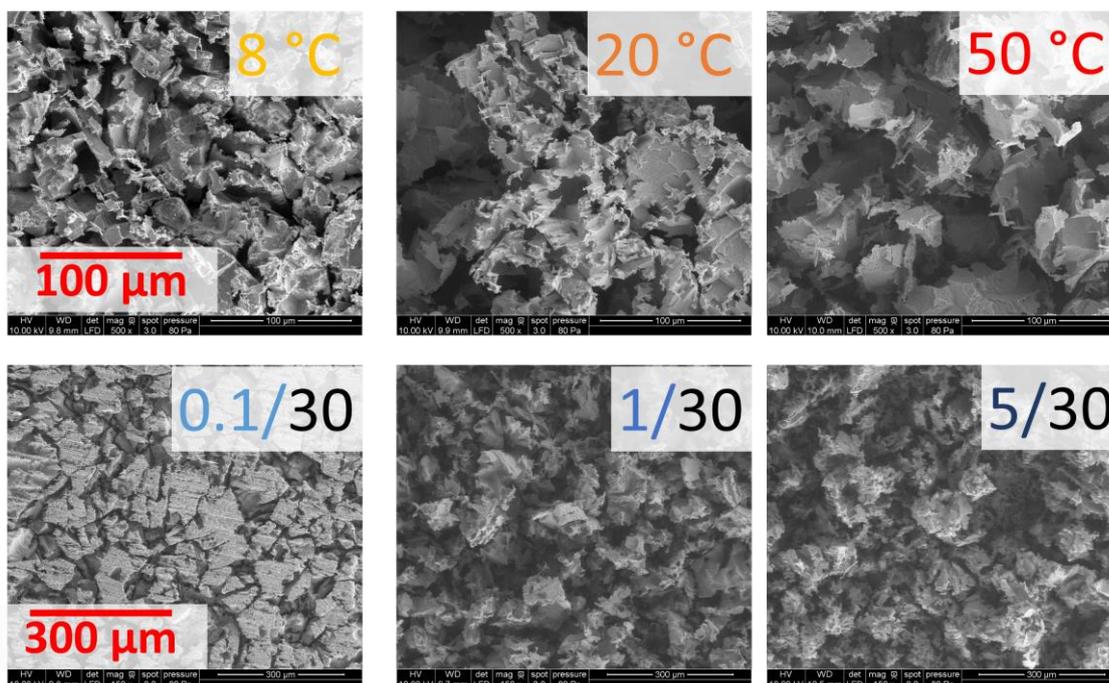


Fig. S1: Surface E1: influence of the temperature of reaction (top row) and concentration (bottom row, in grams) of the HCl- FeCl_3 solution on the texture of the surface.

The wettability and roughness are characterized in Fig. S2 for surfaces $E1$ and $E2$, as a function of the time in the reactive bath. The static contact angle of a water drop on the surface θ^* was measured with a goniometer, as well as the hysteresis $\Delta\theta$ (difference between the advancing θ_A and receding angle θ_R). For both surfaces, the receding angle is always equal to $\approx 0^\circ$ and is not plotted. Superhydrophobic properties were obtained with the HCl/ FeCl_3 ($E1$) or with the HCl/ H_2O_2 ($E2$) etchants for reaction times longer 30h. The trend for both surfaces shows that the value of the wetting angle and roughness increase with reaction time. EA is not mentioned here since it is obtained by not one but two reaction times. For the surface EA , the value of the static and dynamic contact angles are $\theta^*=160^\circ$ and $\Delta\theta < 10^\circ$ respectively, as mentioned in Fig. 4.

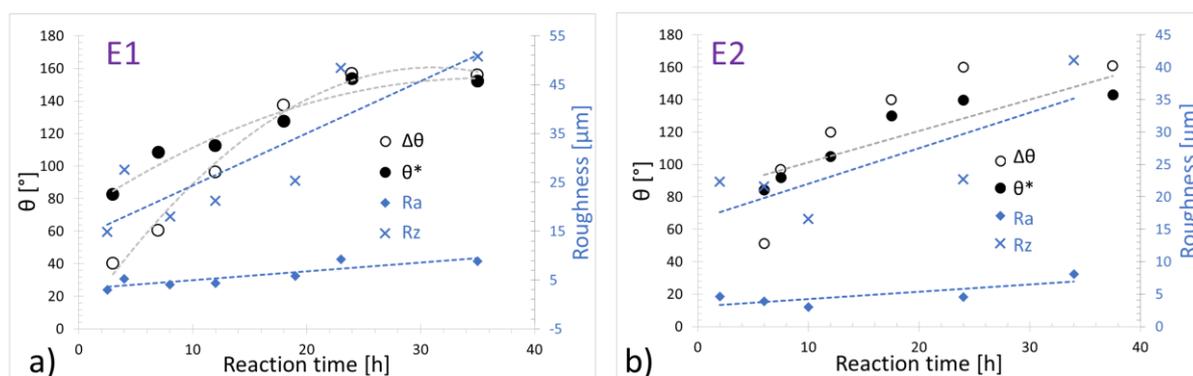


Fig. S2: Influence of the chemical reaction time on the roughness and wettability of the fabricated surfaces. The roughness Ra (arithmetic average of absolute values of the profile height deviations from the mean line) and the height Rz between the lowest peak and the highest valley over a 300 μm length were also plotted. The lines are only plotted as a guide for the eye.

Estimation of roughness and solid fraction

The solid fraction ϕ_s (i.e. the ratio between the solid-liquid contact area and the projected composite area of the interface, see Fig. 3) was measured from SEM images by approximating the structures on $E1$ and $E2$ as cylindrical pillars (Tier 1) with cylindrical micropillars (tier 2

structures), on *EA* are cylindrical pillars (Tier 1) covered with octahedrons (Tier 2 structures) and nanopillars (Tier 3). On the natural surfaces, the first tier of roughness, structures similar to arched structures and separated by lower, darker straight lines on *RL*, “pretzels” shapes on *BL* and dome-shaped pillars on *LL* can be observed. The second tier of roughness, consists of bumps in the case of *RL*, bumps in the case of *BL* and agglomerate of tubular tubes in case of *LL*. A third tier is observed: nano-grass in the case of *RL*, nano-pillars in the case of *BL* and nano-tubes in the case of *LL*.

The values of a , w and p defined in Figure 3 were obtained experimentally as follows. The arithmetic roughness R_a was measured 6 times at 6 different locations on the samples (one scan per location) on a $\sim 250 \mu\text{m}$ scan length with a 3D microscope (Hirox KH-8700, with 100nm optical resolution). The average height a of the features for tier 1 was obtained by assuming that $a=R_a$. For tier 2 and 3, the average height a of the structures was measured on SEM digital images using the software ImageJ⁷¹. The average center to center p spacing between the features for each tier was measured from SEM digital images using the software Image J, assuming that the surface is wavy with wavelength $p=2\pi/k$. Finally, to obtain the width w , we measured the area A of the top of each pillar from SEM digital images using the software Image J. Then by assuming that we have cylindrical pillars, $w = 2\sqrt{A/\pi}$. The values of p , a and w shown in table S1 and obtained with the software ImageJ result from averaging at least 40 measurements of p , a and w respectively. The standard deviation on these at least 40 measurements is also reported in Table S1.

With the values of p and w shown in the Table S1, we can also estimate the solid fraction φ_s and the gas fraction φ_g , according to the equations mentioned in Fig. 3. Results are shown in the last two columns of Table S1.

	Tier 1			Tier 2			Tier 3			φ_s	φ_g
	$p \pm \Delta\sigma$ [μm]	w/p $\pm \Delta\sigma$	a/p $\pm \Delta\sigma$	$P \pm \Delta\sigma$ [μm]	w/p $\pm \Delta\sigma$	a/p $\pm \Delta\sigma$	$P \pm \Delta\sigma$ [μm]	w/p $\pm \Delta\sigma$	a/p $\pm \Delta\sigma$		
Surface E1	27 \pm 9	0.35 \pm 0.41	1.87 \pm 0.87	0.81 \pm 0.4	0.36 \pm 0.75	0.62 \pm 1.46	X	X	X	0.016	0.984
Surface E2	14 \pm 6	0.5 \pm 0.72	3.02 \pm 1.78	0.81 \pm 0.4	0.36 \pm 0.75	0.62 \pm 1.46	X	X	X	0.032	0.968
Surface EA	75 \pm 25	0.32 \pm 0.39	0.67 \pm 0.88	5.88 \pm 2.07	0.63 \pm 0.43	0.63 \pm 0.43	0.41 \pm 0.16	0.68 \pm 0.43	1.13 \pm 0.74	0.018	0.982
Surface RL	217 \pm 19	1	0.39 \pm 0.13	5.22 \pm 1.76	0.58 \pm 0.3	0.58 \pm 0.3	0.45 \pm 0.14	0.20 \pm 0.11	0.20 \pm 0.11	0.013	0.987
Surface BL	42 \pm 11.5	0.31 \pm 0.17	0.16 \pm 0.08	8.99 \pm 2.95	0.44 \pm 0.38	0.44 \pm 0.38	2.75 \pm 1.06	0.26 \pm 0.24	0.13 \pm 0.12	0.001	0.999
Surface LL	13.7 \pm 4.7	0.58 \pm 0.33	0.75 \pm 1.85	1.85 \pm 0.43	0.61 \pm 0.31	0.61 \pm 0.31	0.47 \pm 0.26	0.31 \pm 0.22	1.74 \pm 1.37	0.012	0.988

Table S1: Values of the pitch p , width w estimated experimentally by post-processing of the SEM images in ImageJ. Values of height a are taken as the roughness R_a measured with a 3D microscope, with height resolution below 1 μm . $\Delta\sigma$ is the standard deviation of the experimental values (p , w and a). The values of φ_s and φ_g are also indicated.

Drop impact measurements

The ability of the surfaces to repel water droplets has been investigated by carrying out droplet impact experiments as shown in Fig. S3. A 7 μL water droplet was repeatedly impacting on the copper surfaces bare, *E2* and *EA* at different heights, to quantify the highest sustainable pressure by the surface before break-in. Each drop volume is controlled by using a syringe pump that is connected with a plastic tubing (Internal diameter of 3mm) to a 30G needle pointing to the surface. For the experiments on the surfaces *RL* and *BL*, the leaf was maintained using a “helping hand” (mini plier) and the free fall height of the droplet was varied up to 1.8m (maximum height that can be attained by the setup). The droplet size has also been controlled from 7 μL to 25 μL to reach higher values of the impact velocity in the case of *RL* and *BL*. The camera used to capture this image sequence is a Redlake HG100K, shooting at 3000fps at a resolution of 800x600 pixels,

and an exposure time of 40 μs . The surface *EA* was shown to repel water up to an impact velocity equal to 2.1 m/s ($We \approx 150$ and $Re \approx 5000$), which corresponds to a height of free fall of $\approx 40\text{cm}$ for the $7\mu\text{L}$ droplet while *E1*, *E2* and the bare copper surfaces were not shown to repel any water droplet. The surface *BL* and the surface *RL* were shown to repel a $25\mu\text{L}$ water droplet (diameter equal to 4.8mm) even for the highest height investigated here (1.8m), which corresponds to a maximum velocity equal to 5.2 m/s ($We \approx 1700$ and $Re \approx 23000$). The compliance of the leaf and the elasticity of the microstructure may help for superrepellency.

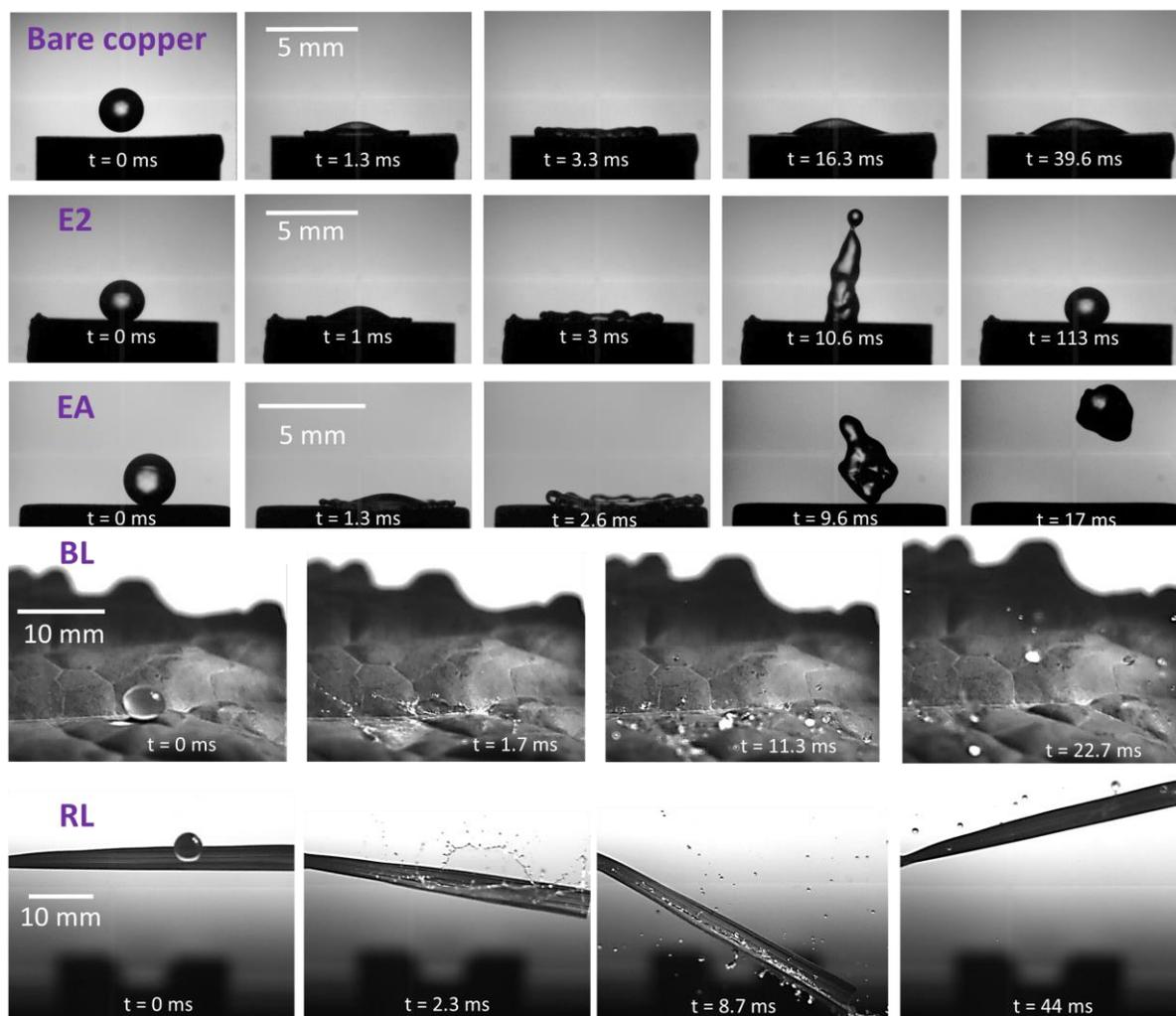


Fig. S3: Sequence showing the comparison between the impact of a $7\mu\text{L}$ water droplet on the bare copper surfaces, on the two engineered surfaces *E2* (high hysteresis $\Delta\theta$) and *EA* (low $\Delta\theta$) falling from a height of 15 cm, and on the two leaves *BL* and *RL* for a $25\mu\text{L}$ falling from 180cm. During this experiment, the Weber number was $We \approx 100$ and the Reynolds number was $Re \approx 1250$. Indeed, the surface *EA* is shown to repel water up to $We \approx 150$ and $Re \approx 5000$ that corresponds to a height of free fall for the droplet of approximately 40 cm. The surface *BL* and the surface *RL* were shown to repel a $25\mu\text{L}$ water droplet (diameter equal to 4.8mm) even for the highest height investigated here (1.8m), which corresponds to $We \approx 1700$ and $Re \approx 23000$.

EDS measurements

To confirm the chemical composition of the surfaces *E1*, *E2* and *EA* fabricated here, an Energy-dispersive X-ray spectroscopy (EDS) analysis has been carried out a few hours after fabrication and 30 days after fabrication (See Fig. S4). Surfaces *E1* and *E2* were shown to have a contact angle hysteresis that decreases with degree of oxidation. In fact, after 30 days, the contact angle hysteresis decreases from $\Delta\theta \approx 150^\circ$ obtained after fabrication to a much lower value $\Delta\theta \approx 55^\circ$. As shown by the EDS measurements in Fig. S4, these oxidized surfaces have a slight increase of oxygen in their chemical content, showing that an oxide has been forming on the surface (the ratio $\text{Cu}/\text{O} = 4/1$). Indeed, with CuO surfaces (ratio $\text{Cu}/\text{O} = 1/1$) the hysteresis is even smaller $\Delta\theta < 10^\circ$. We can therefore suggest that the more oxidized the surface, the smaller the hysteresis. 30 days after fabrication, No change in wettability has been measured on surface *EA*.

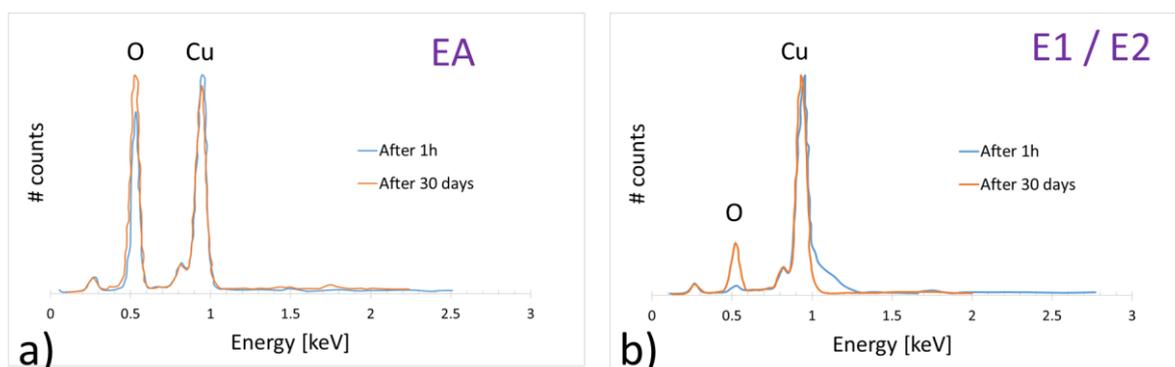


Fig. S4: Chemical composition analysis of the fabricated samples. a) EDS measurements of surface *EA* show that the main composition of the surface is copper oxide CuO , even after 30 days. b) EDS of surface *E2* confirm the chemical nature of Cu surfaces and its stability over 30 days. The EDS analysis of *E1* was also performed and revealed a similar surface composition (compared to *E2*) and is not shown here.

Durability tests

EDS measurements in Fig. S4 show that the surfaces prepared in this work are robust in terms of chemistry. Fig. S5 shows that the contact angle on surfaces *E1* and *E2* is either constant or slightly increasing, over 30 days of exposure to air. Contact angle and hysteresis were measured to remain constant for at least 30 days of exposure to air; this shows the durability of the superrepellency of surface *EA*.

The effect of high temperature on durability of the surface was also quantified, given that superhydrophobic surfaces are of great technological interest in boiling heat transfer³. Fabricated samples *E1*, *E2*, *EA* were subjected to two temperature resistance tests: (a) immersion in boiling water on a hot plate set at 150°C for one hour, and (b) heating in ambient air on a hot plate at 250°C for 10 minutes. The color, visual aspect and wetting angle values of the samples did not change after these tests.

Samples *E1*, *E2*, *EA* and one bare copper sample were also packaged for typical pool boiling experiments, as follows. A surface mount resistor was soldered on the back of each samples, with connection to a power supply (Agilent, N5750A, 750W DC). The sample was epoxied onto a Teflon casing, providing thermal insulation of its sides and back. The package is then immersed in degassed Type II deionized water. Electrical power is then supplied to the heater to maintain nucleate boiling on the sample for at least 20 minutes, before it is set to zero W/cm^2 to start the pool boiling measurement. Then, the heat flux is increased by steps of $\approx 5\text{W}$ and maintained constant for 10 minutes before each data point is recorded. Thereafter, the heat flux is again increased at the same rate to ensure the repeatability of the experiment and obtain the value of the critical heat flux. Hysteresis between the upward and downward boiling curve was found to be negligible on all experiments. The typical duration of a boiling curve measurement was 8 hours.

Contact angles (static and dynamic) were measured on *E1*, *E2* and *EA* before and after pool boiling experiments. No significant change of wettability was observed if critical heat flux had been reached during the experiment. Samples submerged in water for 24 hours at a moderate heat flux were found to be in a hydrophilic Wenzel state, similar to the report on lotus leaf²⁹. Reverting to the metastable superhydrophobic Cassie-Baxter would take about 10 minutes at 120°C , or four to seven days at atmospheric conditions (Iowa autumn is typically dry). Reaching twice the critical heat flux during pool boiling experiments did not alter wettability properties of any sample surface.

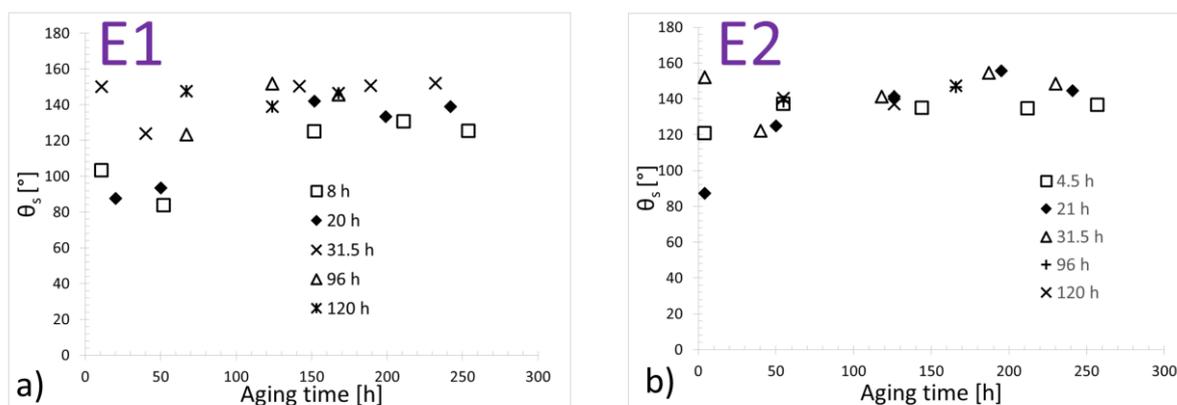


Fig. S5: Measurement of the stability of the samples at ambient conditions. Effect of the time after reaction (aging time on the

x-axis) on the contact angle for samples *E1* and *E2*. The times mentioned as a parameter are the time of reaction of the samples. The effect of the aging time on the contact angle was also measured on *EA* without any degradation of the contact angles.