Observations of Changes in Surface Chemistry of Metallic FLSP Surfaces as a Function of Wettability

Graham Kaufman, Shojan Pavunny, Xiao Zeng, Dennis Alexander, Craig Zuhlke
University of Nebraska - Lincoln

UNIVERSITY of NEBRASKA LINCOLN

CEFS Center for Electro-Optics & Functionalized Surfaces

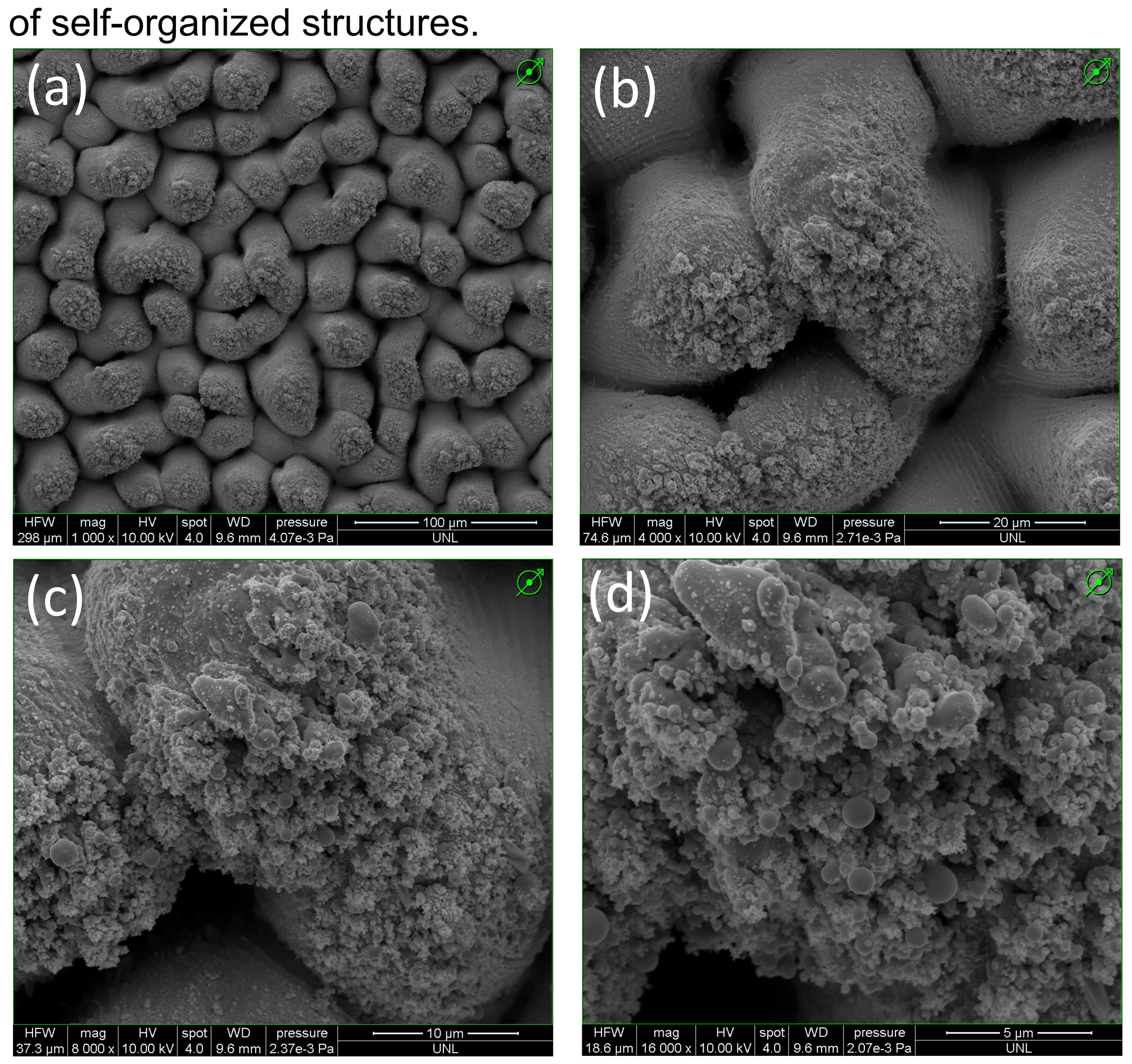
Motivation

Metal surfaces processed with femtosecond laser surface processing (FLSP) have a wide variety of applications. One application is the creation of superhydrophilic or superhydrophobic surfaces on metals. Creating a superhydrophobic surface on an electrical powerline can limit ice build-up during winter storms, potentially saving millions of dollars annually. Metal FLSP surfaces are intrinsically superhydrophilic; however, when exposed to air, the wettability of the surface transitions from superhydrophilic to superhydrophobic. We are interested in investigating what changes in surface chemistry result in these shifts in wettability over time. Here we focus on FLSP applied to aluminum and silver. Silver is investigated because the wetting properties change within hours of exposure to air versus more than a month for aluminum.

Goal: Use surface analysis techniques to study changes in surface chemistry of metal FLSP surfaces as their wettability transitions from superhydrophilic to hydrophobic due to exposure to air.

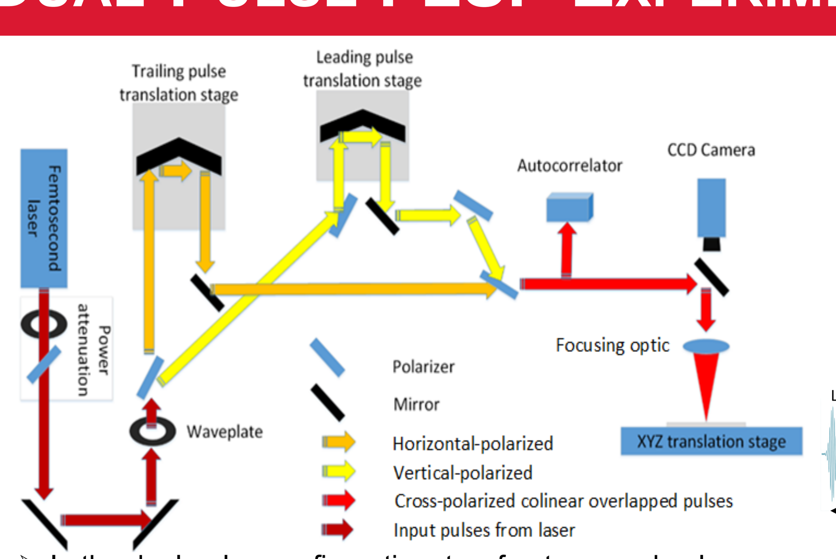
Background on FLSP

FLSP creates dual-hierarchal structuring with micro- and nano-scale features. Intense electric fields from focused, ultra-short laser pulses ablate the metallic surfaces and lead to material removal, surface melts, and redeposition resulting in the formation of self-organized structures.

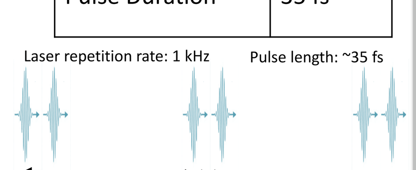


SEM Images of a silver FLSP surface at different magnifications. The surface was made with the following parameters: a peak fluence of 2.9 J/cm^2, a pulse count of 856, and a delay of 120 ps between pulses (see below for explanation of dual-pulse FLSP which is needs to be used to functionalize silver).

Dual-Pulse FLSP Experimental Setup

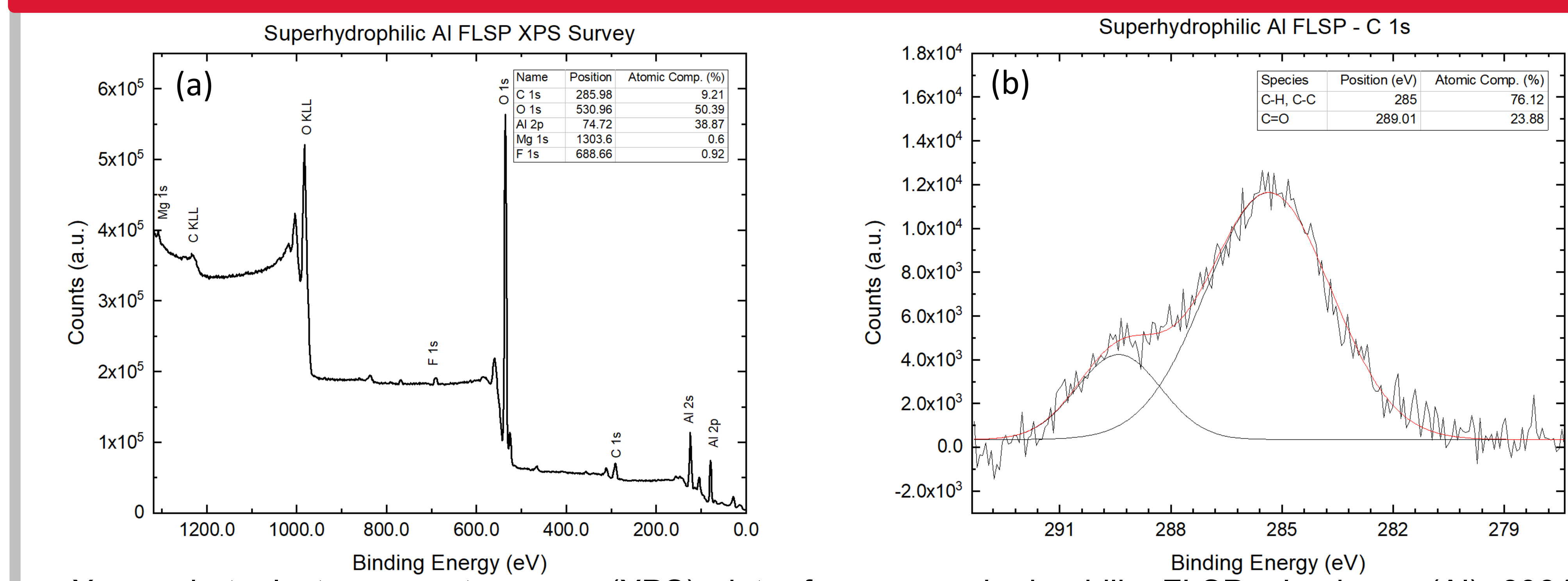


Laser	Coherent Astrella
Pulse Energy	6 mJ
Center Wavelength	800 nm
Repetition Rate	1000 Hz
Pulse Duration	35 fs



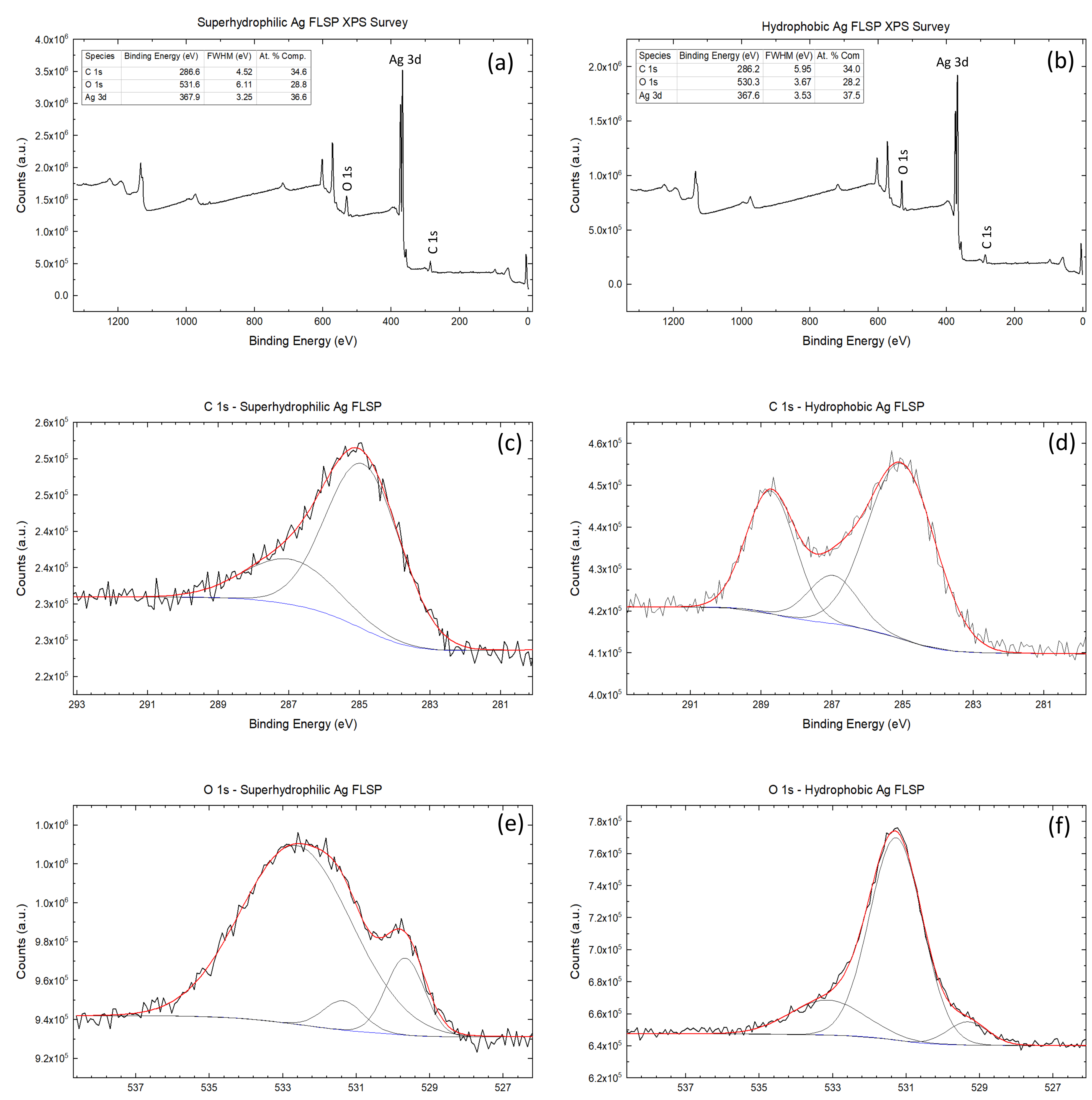
- In the dual-pulse configuration, two femtosecond pulses are spaced < 1 ns apart (pulse-pairs are spaced 1 ms apart based on the repetition rate of the laser).
- Dual-pulse FLSP takes advantage of time dependent light-matter interaction processes.

XPS Data for Superhydrophilic Aluminum 6061 FLSP



X-ray photoelectron spectroscopy (XPS) data for a superhydrophilic FLSP aluminum (Al) 6061 surface. (a) XPS survey scan with percent atomic composition and (b) XPS high resolution C 1s scan showing two main contributions to the C 1s curve at 285 eV and 289 e V.

XPS Data for Superhydrophilic and Hydrophobic Silver FLSP



XPS surveys for (a) superhydrophilic silver (Ag) FLSP sample and (b) hydrophobic Ag FLSP sample with atomic percent compositions for C 1s, O 1s and Ag 3d transitions. High-resolution C 1s scans for (c) superhydrophilic Ag FLSP sample and (d) hydrophobic Ag FLSP sample. The hydrophobic sample has additional contributions in the C 1s curve at 288.8 eV. High-resolution O 1s scans for (e) superhydrophilic Ag FLSP sample and (f) hydrophobic Ag FLSP sample. The ratios of the O 1s components dramatically change from the superhydrophilic to hydrophobic sample. The component at 531.3 eV dominates the hydrophobic signal.

Procedure

- Four samples of both Ag (99.95% pure) and Al 6061 (95% pure) are individually cleaned in a 20-minute sonic bath of acetone, followed by ethanol and finally, distilled water.
- FLSP is applied to the samples using the following parameters:

Laser Parameter	Ag	Al 6061
Delay between pulses (ps)	120	N/A - Single pulse
Laser Spot radius (μm)	270	201
Raster offset or pitch (μm)	40	50
Power (W)	1.65	1.3
Velocity of raster (mm/s)	5.4	4.0
Peak fluence (J/cm^2)	2.9	2.05
Pulse count (pulses)	856	514

- For both Ag and Al 6061, immediately after processing and before the samples have a chance to transition, one sample is placed inside the ultra-high vacuum chamber (UHV) for analysis with XPS and the contact angle is measured for the second sample. Two additional samples, used for hydrophobic experiments, are set under a clean, upside-down petri dish, in open air.
- XPS is performed on the superhydrophilic samples.
- After exposure to air, contact angle is measured on one of the two remaining samples. Once the sample's wettability has transitioned to hydrophobic, the hydrophobic sample intended for analysis is placed into the UHV system and XPS analysis is performed.

Results – Contact Angles

Material	Super-hydrophilic CA	Hydrophobic CA	Unprocessed Contact Angle
Silver (99.95%)	0°	141.1°	80.1°
Aluminum 6061	0°	--	71.3°

Superhydrophilic Ag contact angle (CA) = 0°

Hydrophobic Ag CA = 141.1°

Conclusions

- As metallic FLSP surfaces are left in a lab environment, their wettability transitions from superhydrophilic to hydrophobic (eventually superhydrophobic).
- XPS survey scans show little change in the atomic percent composition of carbon and oxygen on the surface of the Ag FLSP samples as the wettability transitions.
- High-resolution scans of the C 1s and O 1s peaks for the Ag FLSP samples show significant changes in the species present as the sample's wettability transitions.
- The hydrophobic Ag FLSP sample contains a carbon species with binding energy 288.8 eV, often associated with carbon-oxygen double bonds.
- The hydrophobic Ag FLSP sample's surface oxygen content is dominated by the species with binding energy of 531.3 eV.

Acknowledgements

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