

PRF#: 57019-DNIS

Fundamental Investigation of Scale Formation and Corrosion on Hydrophobic and Oleophobic Coatings, and Their Role on Coating Degradation

Nenad Miljkovic, Department of Mechanical Science and Engineering, University of Illinois

The main goal of this project was to create multifunctional nanoengineered surfaces to manipulate fluidic and heat transport processes for robust and long-lasting high performance thermal management solutions which utilize both high (water) or low (refrigerant) surface tension fluids. Thermal management is a critical bottleneck for the advancement of a variety of important petrochemical systems. Phase-change based microfluidic systems promise compact solutions with high-heat removal capability. However, challenges in implementation lead to poor heat transfer performance in both the evaporator and condenser. More recently, multifunctional nanoengineered surfaces have been developed that can significantly enhance the stability and performance of these systems using thin film evaporation, dropwise and jumping-droplet condensation. Although proven in lab scale environments, the wide spread utilization of these surfaces has not been successful due to their poor durability. To successfully implement these phase-change based approaches, the first critical step is obtaining the fundamental understanding of the complex degradation mechanisms on such surfaces with a range of working fluids having high and low surface tensions.

Year 2 (2017 to 2018) of the project focused on four main thrusts. First, we wrapped up our volatile organic compound (VOC) based heterogeneous nucleation studies that demonstrated for the first time the high importance of surrounding environment on nucleation. We expanded our work from Y1 to include experiments conducted in the ambient environments of Fukuoka, Japan and Beijing, China to verify and contrast environmental conditions on the agglomerate formation mechanism. The insights gained from this first study elucidate fundamental aspects governing the behavior of both short and long term heterogeneous nucleation on hydrophobic surfaces, suggest previously unexplored microfabrication and air purification techniques, and present insights into the challenges facing the development of durable dropwise condensing surfaces.

In a second an parallel thrust, we expanded the VOC work as a means to develop structured surfaces that maintain superhydrophobicity without the need of weak coatings. Superhydrophobicity can be obtained via the roughening of an intrinsically hydrophobic surface, the creation of a re-entrant geometry, or by the roughening of a hydrophilic surface followed by a conformal coating of a hydrophobic material. Intrinsically hydrophobic surfaces have poor thermophysical properties such as thermal conductivity, and thus are not suitable for heat transfer applications. Re-entrant geometries, although versatile in applications where droplets are deposited, break down during spatially random nucleation and flood the surface. Chemical functionalization of rough metallic substrates, although promising, is not utilized due to the poor durability of conformal hydrophobic coatings. In this thrust, we developed a radically different approach to achieve stable superhydrophobicity. By utilizing laser processing and thermal oxidation of copper to create a high surface energy hierarchical copper oxide (CuO), followed by repeatable and passive atmospheric adsorption of hydrophobic VOCs, we show that stable superhydrophobicity with apparent advancing contact angles $\approx 160^\circ$ and contact angle hysteresis as low as $\approx 20^\circ$ can be achieved. To gain an understanding of the VOC adsorption physics, we utilized X-Ray Photoelectron and Ion Mass Spectroscopy to identify the chemical species deposited on our surfaces in two distinct locations: Urbana, IL, USA and Beijing, China (Figure 1). To demonstrate the stability of the coatless surfaces during heterogeneous nucleation, we used high-speed optical microscopy to show stable coalescence induced droplet jumping. This work develops an approach to ensure passively durable hydrophobic surfaces through the use of surface roughening only. The work also sheds light on the key role played by the atmosphere in governing interfacial transport and wetting. See Attachment Figures 1 to 6.

The third thrust was a collaborative effort to develop thin film condensation, which utilizes a promoter layer not as a condensation surface, but rather to confine the condensate within a porous biphilic nanostructure. We used nickel inverse opals (NIO) with a thin (<20 nm) hydrophobic top-layer of decomposed polyimide. We demonstrate filmwise condensation confined to thicknesses <10 μm . To test the stability of thin film condensation, we performed condensation experiments to show that at higher supersaturations ($0.975 < S < 2.05$), droplets coalescing on top of the hydrophobic layer are absorbed into the superhydrophilic layer through coalescence induced transitions. Through detailed thermal-hydrodynamic modeling, we show that thin film condensation has the potential to achieve heat transfer coefficients approaching ≈ 100 kW/m^2 while avoiding durability issues by significantly reducing nucleation on the hydrophobic surface. The work presented here develops an approach to potentially ensure durable and high performance condensation comparable to dropwise condensation.

Lastly, the fourth and largest thrust has focused on developing a mechanistic understanding of fundamental degradation mechanisms in thin hydrophobic polymer films that can be used in petrochemical applications for anti-

corrosion and anti-fouling applications. Through the use of films with varying adhesion ($10 - 200 \text{ mJ/m}^2$), thickness ($10 \text{ nm} - 1 \text{ }\mu\text{m}$), and elastic modulus (500 MPa), we identified the formation of stable blisters at nanoscale defects owing to a Laplace pressure mediated mechanism (Figure 2). Using rigorous adhesion theory of films coupled with mass transfer analysis, we show that polymer film degradation during condensation initiates at nanoscale defects, grows via condensation beneath the coating, and expands via a cyclic Laplace pressure mediated mechanism. To characterize our surfaces and verify our theory, we use nanoindentation experiments and optical interferometry to obtain exact blister profiles. This work represents the first mechanistic understanding of hydrophobic coating failure on smooth surfaces and offers design guidelines for future coating development.

The project funded five full-time graduate students (not simultaneously). Due to the heavy experimental nature of the project, all students have received training in surface science characterization techniques at the Material Research Laboratory and Micro-Nano Manufacturing Systems Lab. Examples include: Scanning Probe Microscopy, Scanning Electron Microscopy, Atomic Force Microscopy, Ellipsometry, Time Domain Thermoreflectance, and microfabrication. All students have also partaken in the MRL summer week-long workshop on characterization as well as a weeklong intensive LabVIEW course offered by National Instruments. Furthermore, all students have developed professionally through the attendance of conferences and professional meetings to present their work stemming from this project. Due to significant research progress, one of the students received the Mavis Faculty Fellowship, developed in the College of Engineering to facilitate the training of the next generation of great engineering professors. Another student was the recipient of the PPG fellowship in 2017, enabling him to establish key research collaborations for this program with chemical engineers at PPG.

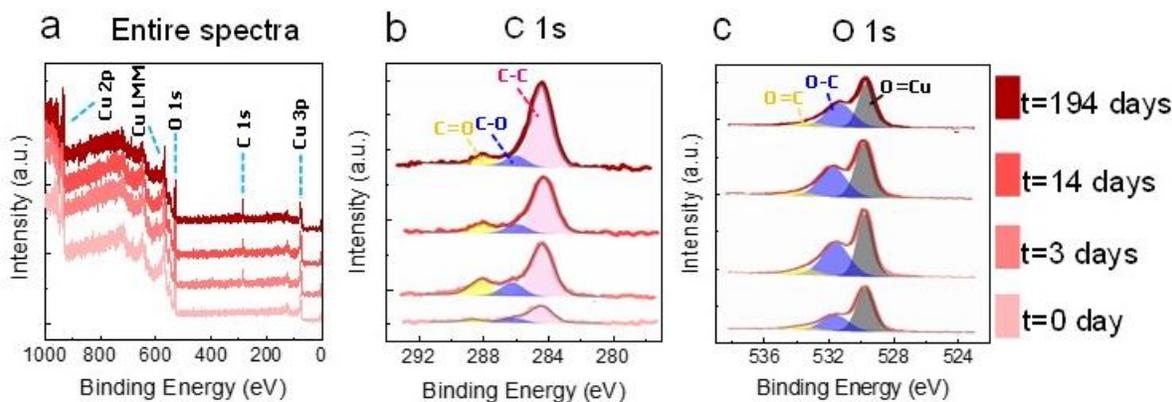


Figure 1. Time-resolved XPS and ToF-SIMS spectra of the hierarchical CuO nanowire surfaces. XPS spectra showing (a) broadband scan results, (b) high-resolution spectra for C 1s, and (c) high-resolution spectra for O 1s. ToF-SIMS positive ion spectrum of the (d) clean hierarchical CuO nanowire surface and (e) atmospherically exposed CuO nanowire surface with 194-day exposure time. The surface in (d) was cleaned by plasma for 3-5 min at a medium power setting.

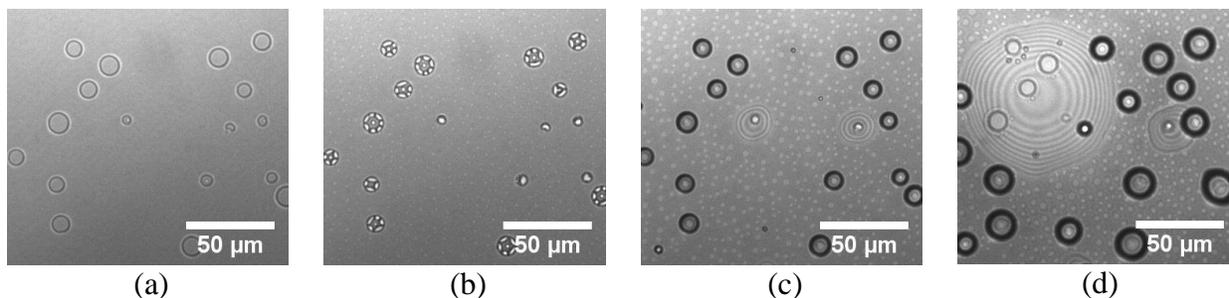


Figure 2. Thermal instability can cause microscale holes growing on polystyrene film on sapphire substrate. Rings of polystyrene will form at the edge of the holes and causes the local thickness to increase. Prior researches pointed out larger rings will have thicker rings. When condensing for 0, 5, 15, 30 seconds (a to d), coating delamination happened on smaller defects ($< 5 \mu\text{m}$) and caused water blister ($r^* < 1$). Defects larger than $5 \mu\text{m}$ will not delaminate the coating (c) ($r^* > 1$). This illustrates r^* was increased with the increase of thickness.