Surface Modifications for Dew Collection

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Background

Clean water is a valuable resource that can be hard to access, especially in the wake of a natural disaster. According to the World Health Organization, an individual requires 2.5-3 liters of drinking water per day in emergency situations, with variation depending on climate and physiology. This number further increases to 7.5-15 liters when hygiene and cooking needs are included.[1] Our senior design project focuses on functional surface coatings that could be used to supplement daily drinking water supply. Specifically, we are focusing on surface coatings designed to collect water from humidity in the air.

Thermodynamic derivations and experiments in literature have shown that water condensation droplets nucleate at a higher rate when the surface has a lower wetting angle.[2,3] Wetting angles are numerically represented as 0° and 180° for completely hydrophilic and hydrophobic surfaces, respectively. In nature, the Namib Desert beetle can harvest moisture from its arid environment via structural and chemical variations on its shell, which result in a pattern of high and low wetting angles.[4] Dr. Shu Yang at the University of Pennsylvania is investigating methods of replicating this naturally occurring material by creating surfaces with highly hydrophilic regions for effective dew collection coupled with superhydrophobic regions to direct the water off of the surface. We also aim to create such a surface, but are using alternative methods and materials from those of Dr. Yang.

Methods

Hydrophilic Treatment

To make copper surfaces hydrophilic, we replicated a technique developed by Huang and Leu.[5] Following their method, copper substrates were first submerged in 15 wt% nitric acid in order to remove surface impurities and the native oxide. After rinsing with deionized water and drying by heating on a hotplate, the substrates were immersed in 30 wt% hydrogen peroxide. This treatment results in the formation of copper oxide nanostructures on the surface of the material, which makes the surface highly hydrophilic. The change in appearance due to this process is visible in Figure 1 to the right.

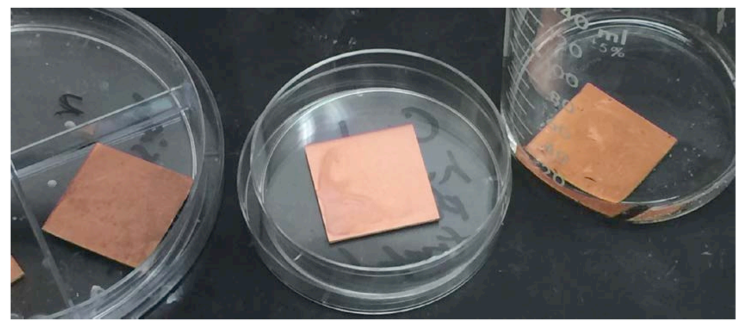

Figure 1. From left to right: Untreated copper, native oxide removed with nitric acid, and treated by hydrogen peroxide

Hydrophobic Treatment

To create a hydrophobic surface, we adopted the technique developed by Larmour, Bell, and Saunders.[6] The method attempts to mimic the double rough surface of a lotus leaf by coating a metal with a textured layer of a second metal. In this case, we coated copper with a textured layer of silver. To do this, the samples were immersed in 0.01M silver nitrate for 2 minutes. Next the samples were immersed for 5 minutes in a 1mM solution of heptadecaflouro-1-decanethiol (HDFT) in dichloromethane. This is intended to cover the surface with a self assembled layer of non-polar molecules to make the substrate hydrophobic. Figure 2 depicts the refinement of our technique.

Figure 2. From top to bottom: Hydrophobic coatings, increasing in uniformity

Device

To create a device on which dew could condense and then be directed for collection, we layered hydrophilic copper mesh on top of a bulk hydrophobic copper substrate (Figure 3). Our hypothesis was that water would condense onto the hydrophilic mesh, and when the droplets become heavy they would fall through the mesh onto the hydrophobic surface and roll off. We investigated the effectiveness of 3 different grades of mesh (from coarsest to finest: 22 Mesh 0.015, 30 Mesh 0.012, 50 Mesh 0.009). We also investigated an alternative to the mesh layer device. In this second method, we treated a copper substrate to be hydrophilic and then used the adhesive part of a Post-it Note as a mask to create a striped pattern of exposed and unexposed regions on the surface (Figure 4). The masked sample was then treated to be hydrophobic .

Characterization

We characterized the surfaces in several ways. First, we examined surface topography with scanning electron microscopy (SEM) and measured water contact angles using ImageJ software. We also performed rolling droplet tests on a roof-like setup at 45° to the horizontal (Figure 3). In this setup, we deposited 25 µL of water at a time onto the inclined surface and counted the number of drops needed before water fell off of the bottom edge of the sample.

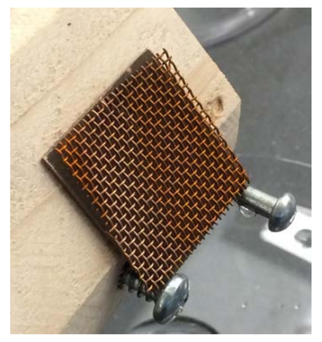

Figure 3. Roof-like setup for 30 Mesh 0.012 (hydrophilic) layered on hydrophobic substrate.

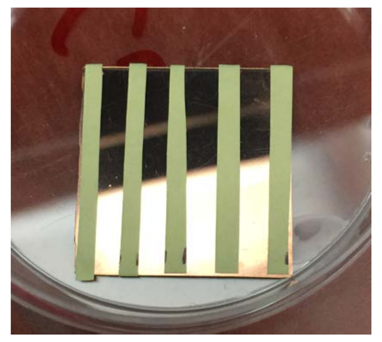

Figure 4. Cut Post-it notes acting as mask, before hydrophobic treatment

Results

Unmodified Substrate

An SEM micrograph of an unmodified substrate is pictured in Figure 5(a). As shown, the surface is coated by its native oxide, with regions where the oxide has been damaged. The water contact behavior for such substrates are shown in Figure 6(a). The average contact angles measured for unmodified copper is 84°. Rolling droplet testing for such substrates required an average of four 25 µL droplets for the water to roll off of the surface (rolling droplet test results are summarized in Figure 9).

Hydrophilic Substrate

SEM micrographs of the copper samples treated to be hydrophilic reveal the presence of very fine nanostructures that are likely copper oxide (but the chemistry has not been verified). These structures are shown in Figure 5(b). The water contact behavior of these surfaces is drastically different from the unmodified surfaces and is illustrated in Figure 6(b). Average contact angles for these surfaces are 22°, confirming their hydrophilicity. During rolling droplet tests, the average number of droplets needed for the water to roll off of the surface is 17.5.

Hydrophobic Substrate

The first several samples we attempted to make hydrophobic exhibited limited hydrophobicity; the surface coatings were not uniform and the highest achieved contact angle was around 140°. SEM micrographs of these suboptimal surfaces showed that the first step of our wet chemical procedure indeed deposited a layer of cubic crystals about 300 nm in width (Figure 5(c)), but the second step of treating in HDFT and dichloromethane did not uniformly affect the surface. The water contact behavior of these surfaces is shown in Figure 6(c). We found that leaving more time for the samples to dry between these two steps yields surfaces that are more uniformly coated with HDFT, as shown in the SEM micrograph in Figure 5(d). We are not able to capture the water contact angle on these hydrophobic surfaces because water immediately beads up and rolls off of them. Hence, we assume that the water contact angle approaches 180°. Note that the image in Figure 6(d) does not show the true contact angle because the droplet is still adhered to the needle.

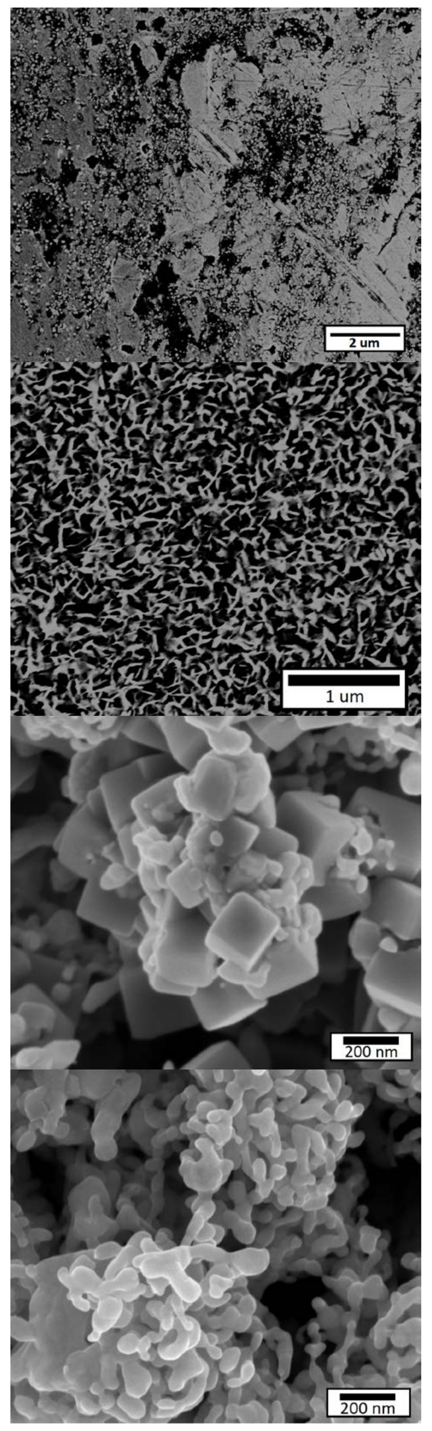

Figure 5 (left). SEM micrographs of (a) unmodified copper surface, (b) hydrophilic surface, (c) semi-hydrophobic surface showing cubic nano-crystals deposited on copper substrate, and (d) super-hydrophobic surface

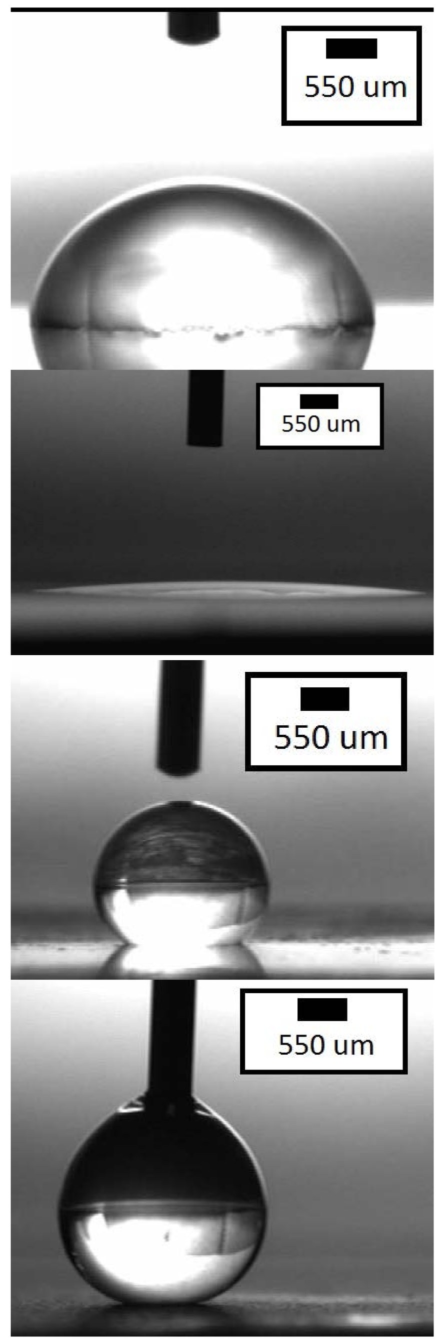

Figure 6 (right). Wetting behavior on (a) unmodified copper surface, (b) hydrophilic copper surface, (c) semi-hydrophobic copper surface, and (d) superhydrophobic surface.

Mesh and Substrate Layering

When we performed rolling droplet tests on the layered devices (as depicted in Figure 3), we found that water was trapped by the mesh and did not easily roll off of the devices. With a small variation depending on mesh grade, 7 to 8 drops were needed before any water dripped off of the device. This layered design is thus ineffective for collecting water.

Post-it Note Masking

Using the adhesive part of Post-it Notes, we were able to create effective masks with which to pattern copper substrates. We masked both an untreated polished copper surface as well as a treated hydrophilic copper surface and then treated both according to our hydrophobic procedure (Figure 7). We found that the Post-its stayed adhered to the polished copper during the first step of the procedure but detached during the second. However, the HDFT cannot bond to the substrate without the deposited silver nanocrystals, and as a result the surface only became hydrophobic in the originally unmasked regions. The Post-its stayed adhered to the hydrophilic surface throughout the procedure. The result was a pattern of hydrophilic and hydrophobic regions on the surface (Figure 8).

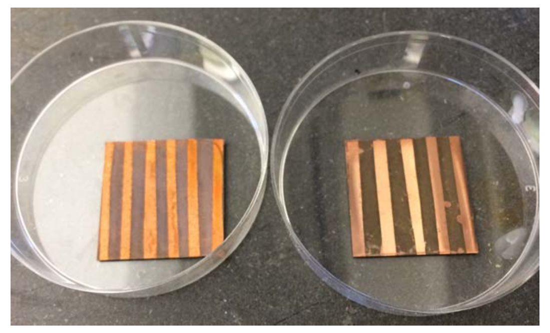

Figure 7. Left: sample treated to be hydrophilic before masking and hydrophobic treatment. Right: untreated polished copper after masking and hydrophobic treatment.

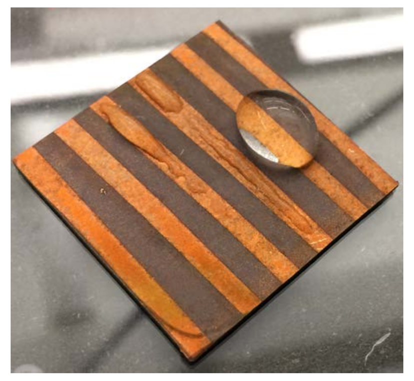

Figure 8. Hydrophilic-hydrophobic striped pattern on copper substrate with a droplet of water adhered to a hydrophilic region.

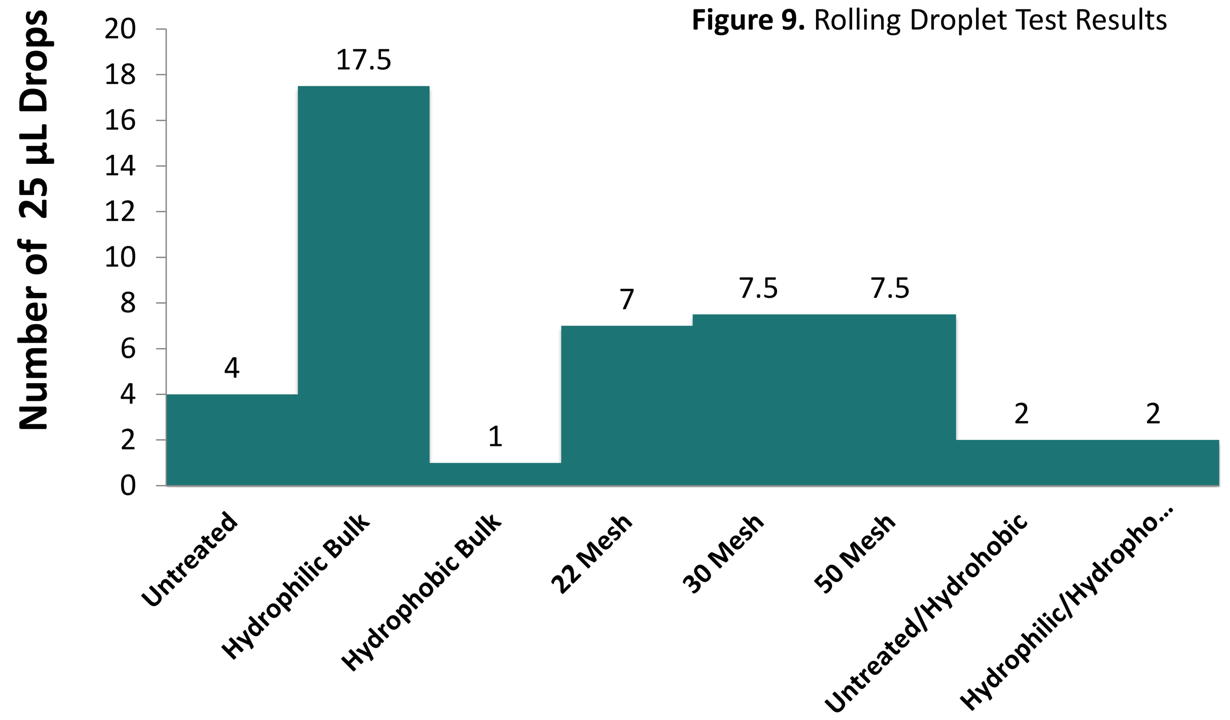

Figure 9. Rolling Droplet Test Results

Conclusion

We conclude that the layered mesh-substrate construction is not ideal for water collection because the hydrophilic mesh traps the water, preventing it from rolling off of the hydrophobic surface underneath. In our subsequent investigation, we found that Post-it Notes were an effective mask and did not damage the hydrophilic surface upon removal. The result was a copper substrate with a striped pattern of hydrophilic and hydrophobic regions. The effect of different masking pitch and width sizes would be an interesting area for future investigation. Moreover, a crisscrossed pattern would better mimic the structure of the Namib desert beetle. In addition, placing the samples on top of a thermoelectric cooler inside a humidity chamber may be a good way to simulate dew formation conditions in nature, and would be a viable experimental setup for testing water collection on further iterations of these patterned devices.

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