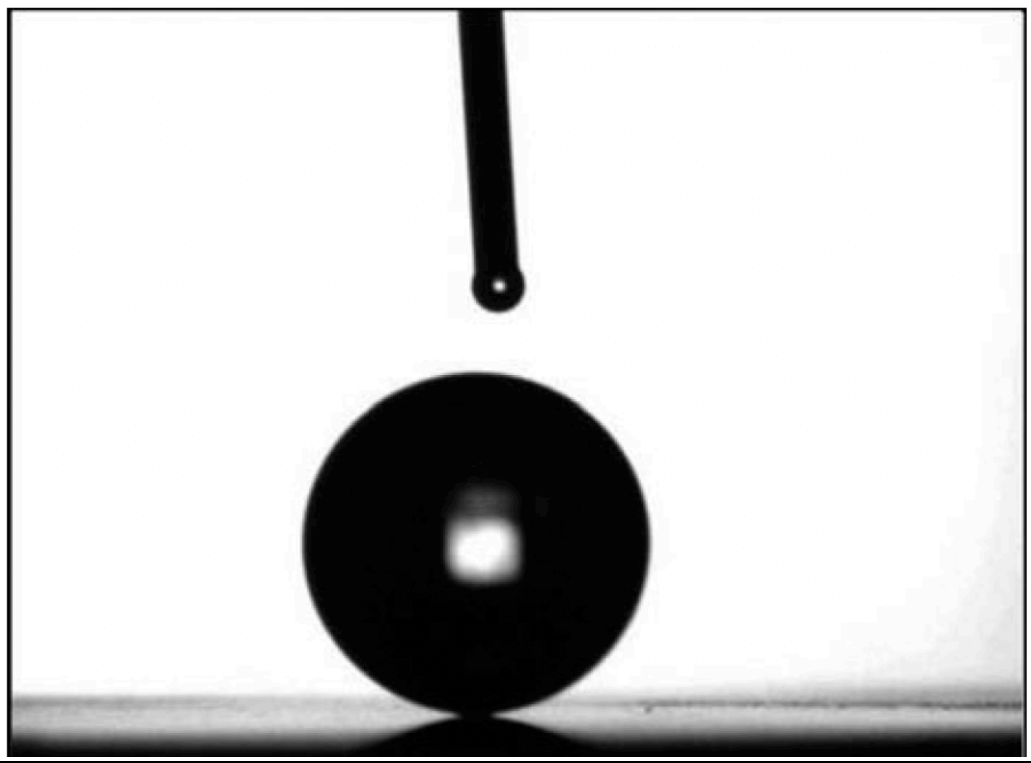


Simple Fabrication of a Superhydrophobic Surface

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Lab Materials

Polished copper sheet	1 sheet per class	McMaster Carr P/N 8894K28
400 grit sanding pad	3 pads per class	McMaster Carr P/N 4611A166
600 grit sanding pad- 3/lab	3 pads per class	McMaster Carr P/N 4611A165
800 grit sanding pad – 3/lab	3 pads per class	McMaster Carr P/N 4611A164
1200 grit sanding pad - 3/lab	3 pads per class	McMaster Carr P/N 4611A163
1800 grit sanding pad - 3/lab	3 pads per class	McMaster Carr P/N 4611A162
Heptadecafluoro-1-decanethiol (HDFT)	1 gram per class	Sigma Aldrich PN 08686-1G-F
0.01 molar Silver nitrate (AgNO_3)	1 liter per class	Sigma Aldrich P/N 34294-1L-R
Dichloromethane (CH_2Cl_2)	1 liter per class	Sigma Aldrich P/N 270997-1L

Plus these general laboratory items:

De-ionized (DI) water	Pyrex beakers, 50 ml (1 dozen / 9 students)
Tweezers	Timer
MicroPipette (5-50 micro liter range)	Double sticky tape
Safety glasses/goggles	Chemical handling gloves
Digital Angle Locator	Amazon.com: Johnson 40-4064

Instructor Pre-Lab Preparation

- Cut/shear copper into ~ 2 x 5 cm pieces (1 / three students)
- Prepare polishing stations

In the wet lab, for each of the three student teams:

- Add 40mL of silver nitrate (AgNO_3) to **Beaker 1**.
- Add 40mL of **DI** water to **Beaker 2**.
- Add 40mL of dichloromethane (CH_2Cl_2) to **Beaker 3**.
- Add 40mL of dichloromethane (CH_2Cl_2) to **Beaker 4**.

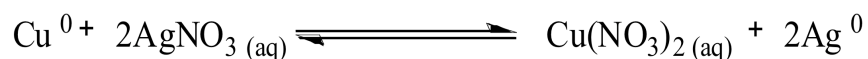
Introduction

This lab is taken from the work done by Iain A. Larmour et al. ¹ on fabricating **superhydrophobic** surfaces. Research on **hydrophobic** materials has been motivated by the nature of lotus leaf. Scientists show that the hydrophobicity of the lotus leaf comes from the micro and nano roughness on its surface. There are countless efforts on fabricating superhydrophobic materials. Some of the artificial surfaces are made from polymers, carbon nanotubes, and metals. There are numerous applications for hydrophobic materials such as non-stick surfaces for cooking, low water resistance surfaces for speedboats, and self-cleaning windows.

In this lab, students will fabricate a simple superhydrophobic surface on a copper sheet, using chemicals purchased from Sigma Aldrich. This process is very fast and straightforward composed of two main steps.

Step 1: Producing a nano-roughened silver surface

This step involves a simple reaction between copper and silver nitrate, producing nano-roughened silver surface on copper. The following equation explains this reaction:

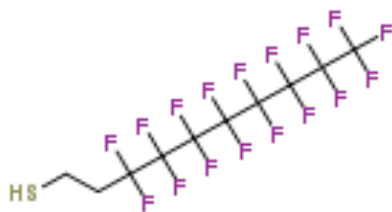


In this reaction, the silver ion (Ag^+) in silver nitrate becomes reduced by the copper surface, forming silver metal.

Step 2: HDFT monolayer self-assembly

In the second step, the silver-coated copper is dipped in a 1 mM heptadecafluoro-1-decanethiol (HDFT) solution.

The purpose of this step is to leave a self-assembled monolayer with non-polar (and thus hydrophobic) molecular segments at the upper surface.



<http://www.chemspider.com>

Figure 1. Chemical structure of HDFT.

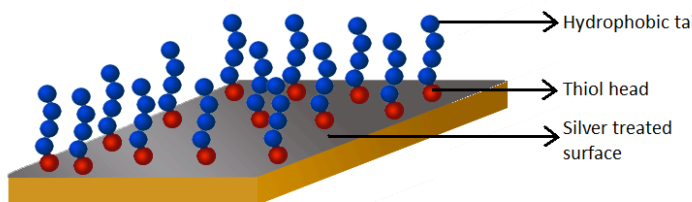
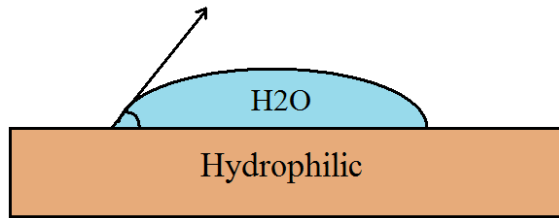


Figure 2. Self assembled monolayer made of HDFT molecules.

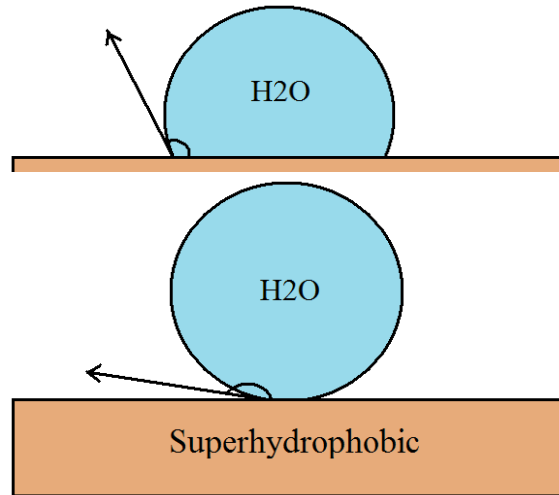
Keywords

Hydrophilic surface--- surface “loves” droplets. The surface maximizes its water, leading to a contact angle of less than 90°.



water contact with than 90°.

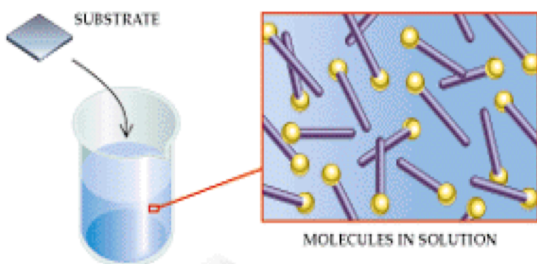
Hydrophobic surface--- surface “fears” droplets. The surface minimizes its contact with water, leading to a contact angle of greater than 90°.



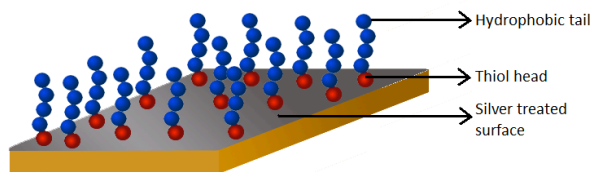
water contact greater than 90°.

Superhydrophobic surface--- surface has nano-scale roughness, leading to contact angle of greater than 150°.

Self-assembly - it is a bottom-up approach for coating surfaces. In this process, the individual molecules template themselves on the surface and form a dense monolayer. Self-assembled monolayers can “functionalize” a surface and make it hydrophobic or hydrophilic. During the second step of this lab, thiol head groups of the heptadecafluoro-1-decanthiol (HDFT) molecules form chemical bonds with the silver nanoparticle surface, which holds the molecule on the substrate. The backbone of the molecule is the hydrophobic tail, which changes the functionality of the surface making it hydrophobic.



Reed and Tour Scientific American 2000



Self assembled monolayer made of HDFT molecules.

Pre-Laboratory Assignment / Quiz Question

For the monolayer self-assembly step of this lab, a 1mM solution of HDFT in CH_2Cl_2 will be used.

Working alone (Honor Code applies):

Calculate the volume of HDFT to be added to 40 ml of CH_2Cl_2 to obtain a final concentration of 1mM (The molecular weight of HDFT = 480.18g/mol; density = 1.678 g/ml).

Remember this number (with its units) as you will need it on the pre-lab quiz.

You may refer to the following simple stoichiometry review to help you with this problem.

Simple stoichiometry and concentration calculations:

The concentration of a solution can be thought of as the “strength” of a solution. It is important to know how to figure out the concentration of a solution and to be able to make solutions of known concentrations in order to perform experiments. The concentration of a solution is usually given in molarity. Molarity is the number of moles of solute per liter of solution.

Molarity (M) = moles of solute/liters of solution

The following are two examples of some typical molarity problems:

Example problem #1:

What is the molarity of a solution of 10 g NaOH dissolved in 5000 ml of water? (Molecular weight of NaOH = 40g/mol)

Solution:

- 1) Determine the amount of NaOH in moles:
 $10 \text{ g NaOH} \times (1 \text{ mol}/40\text{g}) = 0.25 \text{ moles NaOH}$
- 2) Find molarity:
Molarity = $0.25 \text{ moles}/5.00 \text{ L of solution} = 0.05 \text{ mol/L}$

Example problem #2:

How many grams of NaCl should be added to 100 ml of water to get a 1M concentration? (Molecular Weight of NaCl = 58.443g/mol)

Solution:

- 1) Determine NaCl amount in moles:
Mole solute = Molarity * Volume
Mole NaCl = $1\text{M} * 0.100\text{L} = 0.100 \text{ mole NaCl}$
- 2) Convert moles of NaCl to grams:
 $0.100 \text{ mole NaCl} (58.443\text{g/mol}) = 5.84 \text{ g NaCl}$

<<http://www.shodor.net/UNChem/basic/stoic/index.html>>

Student Laboratory Procedure

Step 1) Polish one side of a copper sample (one per group of three students):

- Have the “designated polisher” put on gloves
- Go to the “400 grit polishing station”
- Polish copper on 400 grit pad using circular (or even better, figure eight) pattern of motion

Polishing is complete when surface has an absolutely uniform appearance

- Wipe off copper surface with a fresh tissue or wipe (to remove any abrasive)

REPEAT last three steps for 600, 800, 1200, and 1500 grit pads (in that order)

Step 2) Use pliers to bend up one short end of sample, toward polished surface (last ~ 5 mm)

This will mark the polished side and facilitate capture by tweezers

MOVING TO THE WET LAB:

Step 3) Adjust the micropipette to the amount calculated in your pre-lab assignment and add HDFT to Beaker 3.

Then, use the micropipette to lightly stir for several seconds.

Step 4) Create the superhydrophobic surface

Part A)

- Set the timer to 2 minutes.
- Using tweezers, place the copper plate in silver nitrate (Beaker 1) for 2 minutes with the polished side facing up.

The surface should now have a black tint as the nano-textured silver is deposited on the copper plate.

- Remove the copper plate from silver nitrate and rinse in DI water (**Beaker 2**) for 20 seconds.

Be careful when handling the copper plate with the tweezers in order to have minimal scratching on the silver surface.

- Blow dry the copper plate with the nitrogen gun.

Part B)

- Set the timer for 5 minutes.

- Place the dark side of the copper plate facing up in the bottom of **Beaker 3** and let soak in **HDFT** for 5 minutes.

HDFT covers the nano-textured silver coating with a self-assembled monolayer. The low-surface-energy monolayer further increases the hydrophobicity of the surface.

- Remove the plate from **Beaker 3** and place it in dichloromethane (**Beaker 4**), while agitating for 20 seconds.
- Blow dry with the nitrogen gun.

Dichloromethane is an organic solvent that is commonly used in chemistry.

Step 5) Test the superhydrophobic surface with water

Part A)

- Place the copper plate on a folded Kim-wipe with the superhydrophobic surface facing up and spray with DI water.

There will only be one bottle, so share with other groups.

- Take note of the extreme water-repelling property of the surface.

Notice that water droplets will bounce off the surface upon contact due to the extreme repulsive forces between the surface and water.

- Repeat the process with the other side of the plate and note the difference.

Part B)

- Mount surface on the level with double-sided tape.

- Set tilt to 0.0° and add drops of water.
- Increase the slope by small increments, being careful not to move the level, until you find the angle where water droplets begin to roll off of the surface.
- This is the roll-off angle, or slide angle, and is one way to test the level of hydrophobicity of a surface.

Part C)

- Underwater, these surfaces display another superhydrophobic phenomenon. These surfaces repel water so much that a layer of air remains on the surface when it is submerged in water.
- Hold the surface facing you and submerge your surface into the water. It should appear black, just like when out of water.
- Rotate the surface in the beaker so that you are not looking straight onto the surface. When this angle exceeds the critical angle (48.8°), light rays will completely reflect off the air-water interface, and the surface will look like a perfect mirror.

This is the same effect as if you were a few feet underwater and looking at the distant reflective surface.

Time and facilities permitting:

Step 6) Examine surface under SEM

- With the TA's assistance, inspect the surface's microscopic texture with the Scanning Electron Microscope. Here we will compare the surface of an untreated copper with your treated sample.
- Note your observation. Estimate the diameter of the smallest particles.

1. Larmour, I. et. Al., Angew. Chem. Int. Ed. 2007, 46, 1710-1712.