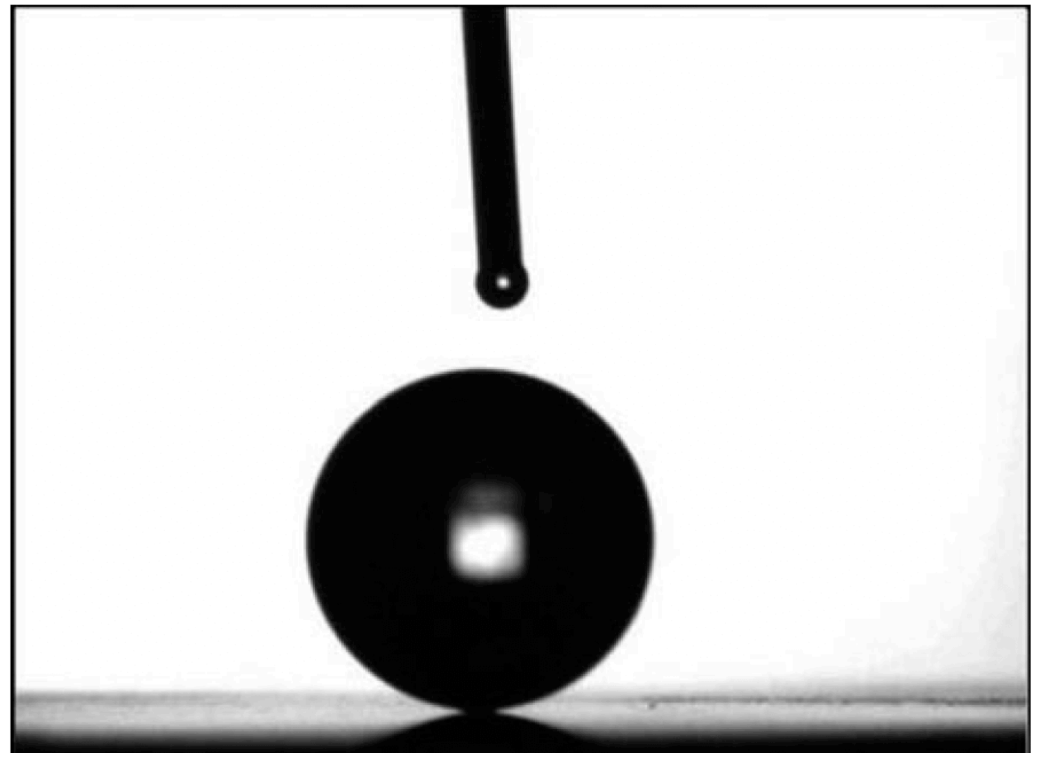
UVA's Hands-on Introduction to Nanoscience

Simple Fabrication of a Superhydrophobic Surface

(revision 22 November – 2013)



This manual for this lab was developed by Kian Keyvanfar David Backer

Lab Materials

Copper sheet - 0.016” x 12” x 12”	1 sheet per class	McMaster Carr P/N 8963K31
500 grit 6” cushioned sanding disc	3 pads per class	McMaster Carr P/N 4521A163 (10 pack)
800 grit 6” cushioned sanding disc	3 pads per class	McMaster Carr P/N 4521A163 (10 pack)
1200 grit 6” cushioned sanding disc	3 pads per class	McMaster Carr P/N 4521A163 (10 pack)
1500 grit 6” cushioned sanding disc	3 pads per class	McMaster Carr P/N 4521A163 (10 pack)
2000 grit 6” cushioned sanding disc	3 pads per class	McMaster Carr P/N 4521A163 (10 pack)
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 (plastic or Teflon coated)	Timer
MicroPippette (5-50 micro liter range)	
Safety glasses/goggles	Chemical handling gloves

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 water-repelling and self-cleaning nature of the lotus leaf. Scientists have shown that the hydrophobicity of the lotus leaf comes from the micro and nano roughness on its surface. Researchers have published countless recipes for emulating this superhydrophobic behavior. Some of the artificial surfaces are made from polymers, carbon nanotubes, and metals. Possible applications include non-stick surfaces for cooking, low water resistance surfaces for speedboats, and self-cleaning windows.

In this lab, you 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:

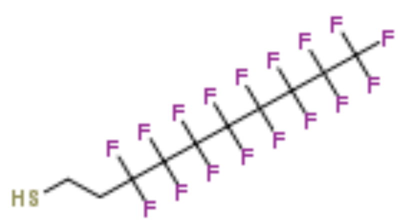
$$Cu^0 + 2AgNO_{3\,(aq)} \rightleftharpoons Cu(NO_3)_{2\,(aq)} + 2Ag^0$$

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.

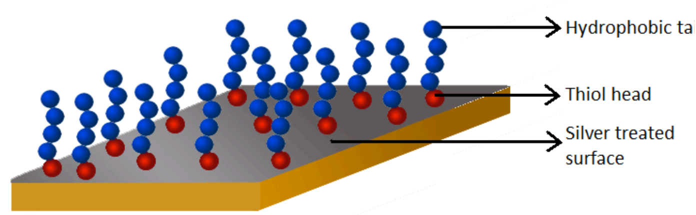
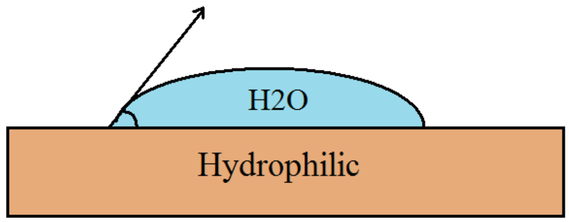
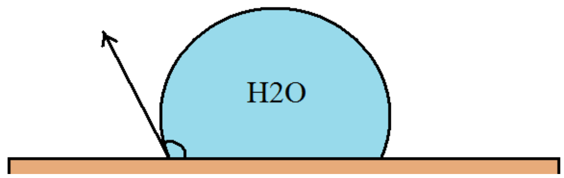


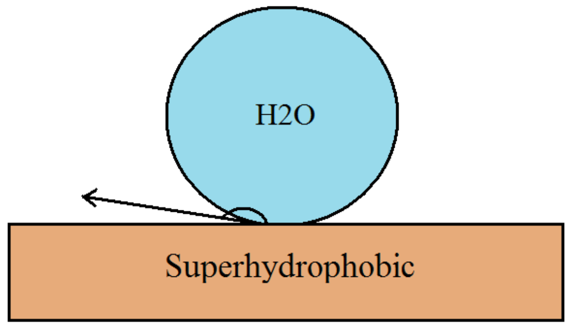
Figure 2. Self assembled monolayer made of HDFT molecules.

Keywords

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



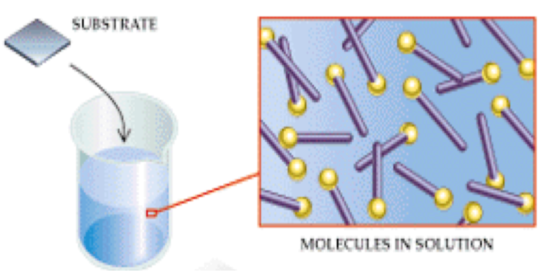




Hydrophobic surface--- surface “fears” water droplets. The surface minimizes its contact with water, leading to a contact angle of greater than 90°.

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

Self-assembly - 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.



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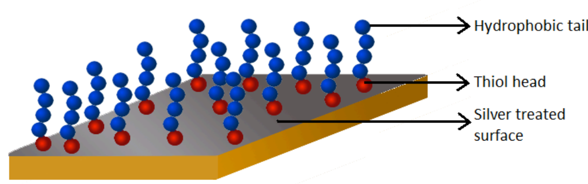

Self assembled monolayer made of HDFT molecules.

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 g NaOH x (1 mol/40g) = 0.25 moles NaOH
2) Find molarity:
   Molarity = 0.25 moles/5.00 L of solution = 0.05 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 = 1M * 0.100L = 0.100 mole NaCl
2) Convert moles of NaCl to grams:
   0.100 mole NaCl (58.443g/mol) = 5.84 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 "500 grit polishing station"

- Put the best face of the copper down on the pad. Place your fingers on top of the copper and polish it by moving in a circular (or figure eight) pattern of motion.

(If the copper won't stay under your fingers, try first lifting up the pad and rubbing it against the copper held in your hand. Once you remove the bigger bumps or ridges, you should be able to put the pad back down and resume polishing with the copper under your fingers)

Check the polishing side of your copper. You may need to shift the position of your fingers to polish the entire copper surface.

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 800, 1200, and 1500 and 2000 grit pads (in that order)

Step 2) Use pliers to bend up one corner of sample toward polished surface (~ 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 4a)

- 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 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 4b)

- 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 (a.k.a PLAY!)

- Water droplet pool/billiards

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

Notice how the droplets bounce off the surface 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.

- Put two or three prepared copper surfaces in a line

Can you get droplets to bounce off the surfaces one after another?

- Super-sized water drops:

Put the tip of the water squeeze bottle almost touching the copper. Slowly squeeze out some water, using the tip to hold the growing drop in one place.

- An instant mirror

If you drop your copper end first into a full beaker of water, what will happen to its water-hating surface?

Now take a look at your copper from the side.

Can you figure out what is going on?

- A boat without a hull

Instead gently set your copper down flat on the surface of a larger water-filled container

What happens?

Try forcing the copper down into the water.

If you do get it to sink, try raising one end back above the water to see what happens.

- Plumbing without pipes (basis for a possible "lab on a chip"):

(Do these experiments last as they will damage your copper sample)

With your tweezers, gently make a small scratch in the center of your copper.

Do water droplets notice what you have done?

With your tweezers, gently scratch a wiggly line down the length of your sample

Slightly raise one end of your sample (by resting one end on something)

Put a water droplet as the high end of you line

Can you get the droplet to run down the path?

Can see how printing patterns in hydrophobic (or phillic) inks might be used to replace pipes (and make miniature chem. labs)?

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.

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