

A Micro/Nano Engineering Laboratory Module on Superoleophobic Membranes for Oil-Water Separation

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ABSTRACT

This article presents a laboratory module developed for undergraduate micro/nano engineering laboratory courses in the mechanical engineering departments at the Massachusetts Institute of Technology and King Fahd University of Petroleum and Minerals. In this laboratory, students fabricate superoleophobic membranes by spray-coating of titania nanoparticles on steel meshes, characterize the surfaces and ability of the membrane to retain oil, and then use these membranes to separate an oil-water mixture. The laboratory module covers nanomaterials, nanomanufacturing, materials characterization, and understanding of the concepts of surface tension and hydrostatics, with oil-water separation as an application. The laboratory experiments are easy to set up based on commercially available tools and materials, which will facilitate implementation of this module in other educational institutions. The significance of oil-water separation in the petroleum industry and integration of concepts from fluid mechanics in the laboratory module will help to illustrate the relevance of nanotechnology to mechanical and materials engineering and its potential to address some of the future societal needs.

INTRODUCTION

In the module, the students fabricate superoleophobic steel meshes by spray-coating of nanoparticle dispersions, separate an oil-water mixture using these meshes, and measure the oil breakthrough height, interfacial tension, surface contact angle, and relate them to breakthrough pressure. Through this module, the students are expected to gain a hands-on appreciation of nanomaterials (titania nanoparticles), methods of surface modification (spray-coating). They will also perform measurements of the interfacial tension to predict breakthrough pressure. Students will take focused well positioned (optical) photographs and use those images to calculate contact angles.

Interfacial forces and hydrostatics

The superoleophobic mesh membrane retains oil because the pressure force imposed by gravity is balanced by the force of oil-water interfacial tension. If the applied pressure on the oil is higher than what the interfacial tension can support, the oil will break through the mesh. The maximum pressure that the interfacial tension can support can be estimated from the Young-Laplace equation [1,2],

$$P_{break} = -\frac{2\gamma_{ow} \cos \theta_{ow}}{d} \quad (1)$$

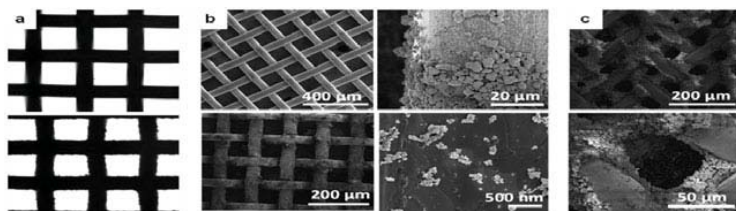


Figure 1. Images of uncoated and TiO₂ nanoparticle coated mesh. (a) Optical images of uncoated (top) and coated (bottom) mesh. (b) SEM images of uncoated (top left) and coated (bottom left) 150 wire/inch mesh, as well as higher magnification images of particle aggregates on the mesh (right). (c) SEM images of coated 250 wire/inch mesh.

where P_{break} is the applied pressure at which oil will break through the mesh, γ_{ow} is the oil-water interfacial tension, θ_{ow} is the oil contact angle with the mesh material in water, and d is the mesh spacing. For gravity-driven filtration, the pressure force created by the weight of the oil column increases with the oil height above the mesh as $P = \rho_o gh$, where P is the gage pressure, ρ_o is the oil density, g is the acceleration due to gravity, and h is the oil column height above the mesh. Thus, the oil column height at which breakthrough occurs (h_{break}) is related to the breakthrough pressure by

$$P_{break} = \rho_o gh_{break} \quad (2)$$

Spray coating is a common technique used in industrial coatings and painting [3]. It is also now commonly used in laboratories to create surface coatings of nanoparticles. The coated surface then acquires some of the properties of the nanoparticles. For example, it has been used to control electronic properties, optical behavior, and wettability [1,3]. Spray coating is a process that can coat large areas with relatively fast drying times [3]. In nanoparticle coatings, the nanoparticles are suspended in a volatile solvent. This mixture is then drawn into a nitrogen stream that is sprayed towards the surface. The mixture becomes dispersed into small droplets in the spray, and the solvent begins to evaporate. These small droplets are scattered over the surface. Because of the high surface-area-to-volume ratio of the droplets, the solvent evaporates fairly quickly, leaving the nanoparticles behind.

Contact angle and interfacial tension measurement

Calculation of the breakthrough pressures (described above) requires values for the interfacial tension and contact angle. It is possible to measure both of these from photographs of droplets. The contact angle can

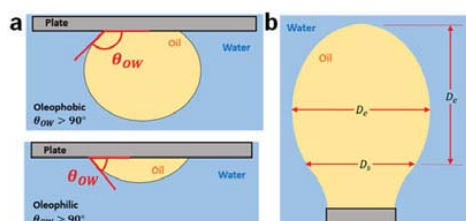


Figure 2. Diagrams defining contact angle (a) and pendant drop method parameters (b).

be measured directly from a photograph of a droplet on a surface. The definition is illustrated in Fig. 2a [4].

The pendant drop method is a way of measuring the interfacial tension [5,6]. By dimensional analysis on a buoyant droplet immersed in another fluid, it can be shown that the shape of the droplet obeys,

$$\frac{\gamma_{ow}}{(\rho_w - \rho_o)gD_e^2} = fnc \left(\frac{D_s}{D_e} \right) \quad (3)$$

where D_e is the maximum droplet width, D_s is the droplet width at D_e from the apex (Fig. 2b), ρ_w is the water density, and the equation has been expressed for an oil droplet in water. The values of D_e and D_s can be measured from a photograph of a droplet with a known scale. Given the functional form above, the interfacial tension can then be calculated.

EXPERIMENT

Step 1: Superoleophobic mesh preparation

First you will spray coat a steel plate for contact angle measurements.

- A 10 mg/mL mixture of 25 nm TiO₂ nanoparticles in isopropanol has been prepared for you. Stir this mixture before use. Fill the glass spray gun jar three quarters of the way full with this mixture (Fig. 3a).
- Attach the top of the container and connect it to the spray gun. Be careful not to turn the spray gun onto its side or let the liquid canister fall off (Fig. 3b).
- Pushing the trigger downward will spray nitrogen. Pushing down and gently pulling the trigger backward will spray some of the mixture with the nitrogen (Fig. 3c). It is only necessary to pull the trigger back part of the way. Make sure everyone in your group is wearing gloves and safety glasses when someone is operating the spray gun.
- Practice spraying the protective backdrop in the fume hood, first with nitrogen, and then with the mixture. Have one person, wearing gloves and safety glasses, hold the steel plate by two corners in the fume hood in front of the protective backdrop. This plate has been pre-cleaned using acetone, ethanol, and water.
- A second person will spray coat the plate. Hold the spray gun in the fume hood, with the nozzle approximately 15 cm from the plate. Start by spraying nitrogen. Gently pull the trigger back to spray the nanoparticle mixture. Scan the spray stream back and forth, top to bottom, over the plate. The entire scan should take about one second.
- After the scan, allow the trigger to return to the forward position, and continue spraying nitrogen over the plate. Scan the nitrogen stream back and forth, top to bottom, watching as the isopropanol evaporates.
- When the plate is dry, repeat the spray coating scan and nitrogen drying cycle. Continue alternating between coating and drying for a total of 10 cycles. Each coating scan should take about one second, and the drying stage should take a little longer.

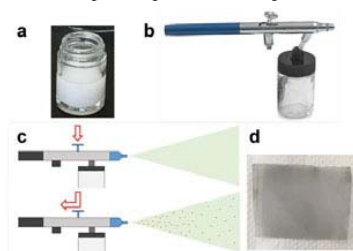
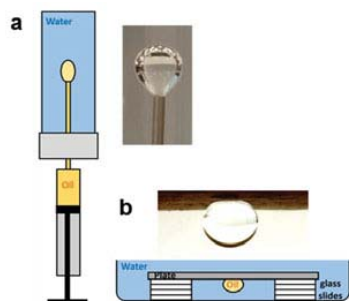


Figure 3. Spray coating. (a) Spray gun jar containing TiO₂ solution. (b) Spray gun with jar connected (source: Ref. 7). (c) Diagram of spray gun operation. (d) Photograph of coated mesh.

h) After the final drying step, set the plate aside on some paper towel. Make sure you can tell which side has been coated.

Next, you will spray coat the steel mesh.

- i) Just as for the steel plate, have one person hold the 150 wires/inch mesh by two corners in front of the protective backdrop in the fume hood. A second person will spray coat the mesh. Again, hold the spray gun in the fume hood with the nozzle approximately 15 cm from the mesh.
- j) In a one second burst, spray coat the nanoparticle mixture on the mesh, scanning back and forth, top to bottom. In between spray coating bursts, allow the mesh to fully dry by spraying nitrogen and scanning back and forth, top to bottom. Alternate between coating and drying for a total of 10 cycles.
- k) After the final drying step, place your mesh in an uncovered plastic Petri dish with your names on it. Place the mesh in the 70°C furnace for at least 15 min to improve adhesion between the nanoparticles and mesh.



Figures 4. Diagrams and photographs of interfacial property measurement experiments. (a) Pendant drop method. (b) Contact angle measurement.

Step 2: Interfacial tension measurement

While your mesh is in the furnace, you will obtain photographs that you will later use to measure the oil-water interfacial tension as well as the contact angle of oil with the steel plate in water.

- a) The apparatus to measure interfacial tension consists of a syringe and needle fitted through the septum of a 20 mL vial. The vial is mounted up-side-down using a ring stand. The vial is filled with water and the syringe is filled with oil (Fig. 4a).
- b) Depress the syringe plunger gradually, until you have a droplet of oil hanging off of the tip of the needle. It may take a few attempts to get a sufficiently large droplet that remains attached to the tip of the needle.
- c) Take a picture of the hanging droplet with the provided camera.

Step 3: Contact angle measurement

You will measure the contact angle of oil with a plate made of the same material as the mesh in water. You will start with the uncoated plate.

- a) The apparatus for measuring contact angle consists of a small dish of water containing glass slides to hold the plate up off of the bottom. Then place an uncoated steel plate on the glass slides (Fig. 4b).
- b) A syringe filled with oil with an attached needle and plastic tube is provided. Position the tube underneath the plate and squeeze out a small drop of oil.
- c) When you obtain a clearly visible droplet sitting underneath the plate, take a photo with the provided camera.
- d) Record the photo number so you can retrieve your photo afterwards. You will use this picture to measure the contact angle.

Repeat this procedure for the nanoparticle coated steel plate.

- e) Make sure to note which photo is for the coated plate and which is for the uncoated plate.
- f) Notice how the nanoparticle coating makes the steel oleophobic.

Step 4: View the mesh in a microscope

- a) Carefully remove your mesh from the furnace.
- b) Examine an uncoated mesh under an optical microscope. You can also obtain a much higher resolution image in a scanning electron microscope (SEM). Acquire photographs and record the photo number.
- c) Then, examine your nanoparticle coated mesh under the microscopes. Take a picture and record the photo number.
- d) SEM images of nanoparticle coated meshes prepared in the same way are provided in Fig. 1.

Step 5: Oil-water separation

You will use your nanoparticle coated mesh to separate an oil-water mixture. As a control experiment, you will first flow the oil-water mixture through an uncoated mesh.

- a) The flow cell (Fig. 5) consists of
 - i. a downstream funnel with a porous disk, on which your mesh will be supported,
 - ii. an upstream column with a funnel that will hold the initial oil-water mixture, and
 - iii. a clamp to secure the mesh between the upstream and downstream sections
- b) The downstream section is supported by a ring stand. Place an uncoated mesh on top of the porous support. Have one person place the upstream section on top of the mesh, and hold it in place. A second person can gently clamp the two sections together.
- c) Pre-wet the mesh by dripping water from a dispenser bottle down the upstream column, directly onto the mesh. Use less than 2 mL of water to do this, but make sure that the entire visible area of the mesh gets wet. The coated mesh is superoleophobic only in water, so this step will be necessary to retain oil.
- d) A mixture is provided of 50% oil by volume, mixed with water colored by blue dye for visibility. Shake the vial to mix it. Take a picture of this initial mixture.
- e) Slowly pour the entire 10 mL vial of the oil-water mixture into the funnel on the upstream side. Avoid pouring the mixture directly down the column, but instead, pour the mixture onto the funnel section and let it gently run down the column. On the uncoated mesh, the oil and water should both go through. You will now remove the mesh from the flow cell.
- f) While holding the upstream column, remove the clamp, and then place the upstream column aside and then remove the mesh and place it aside.
- g) Wipe any excess oil off of the upstream and downstream sections near the ends where the mesh is mounted. Now, you will repeat the flow cell experiment on your nanoparticle coated mesh. Mount the coated mesh in the column as before.
- h) Pre-wet the mesh with water, then gently pour an entire 10 mL vial of the oil-water mixture into the upstream funnel.
- i) You should see the mixture separate (Fig. 5c); the water should pass through the mesh while the oil is retained in the upstream column.
- j) Take a picture of the separated water and oil in the flow cell. Leave the mesh mounted.

Step 6: Breakthrough height measurement

You will now measure the oil breakthrough height for the mesh.

- a) With the mesh still mounted and the separated oil still in the column, pour about 1 mL of pure oil into the funnel on the upstream side.
 - b) Give the oil a little time to run down the column and settle, and observe the height of the oil column. Then, Repeat, pouring about 1 mL of oil at a time, and watching the oil height.
 - c) If the oil comes within 2 cm of the start of the funnel section in the upstream column:
 - a. insert the extension tube (Fig. 5 a,b) in the end of the column, rubber end first,
 - b. gently press the extension tube down to seal it in the column,
 - c. then continue pouring oil into the extension tube, 1 mL at a time.
 - d) Continue pouring oil, 1 mL at a time, until the oil breaks through, and runs out the other side of the mesh. Record the oil column height just before breakthrough.
- To investigate how the forces retaining the oil column are related to the mesh size, you will measure oil breaking height on meshes with 80, 100, 200, and 250 wires/inch.
- e) Dismount the membrane from the flow cell as before. If the extension tube is connected, gently disconnect it from the upstream column before removing the clamp.
 - f) The meshes with 80, 100, 200, and 250 wires/inch have been pre-coated with nanoparticles and baked. Mount one in the flow cell as you did for the other mesh.
 - g) Pre-wet the mesh with less than 2 mL of water, as before.
 - h) This time, you will NOT pour the oil-water mixture through the mesh. Instead, you will pour pure oil, 1 mL at a time from the start.
 - i) Watch the oil height rise, and record the height just before the oil breaks through.
- Repeat this process, measuring the breaking height of each of the 80, 100, 200, and 250 wires/inch meshes.

Visualization of nanoparticle coating

6. Present microscope images of your coated and uncoated 150 wire/inch meshes.
7. Describe any interesting features of the nanoparticle coating from the optical microscope and SEM images. Discuss possible causes of these features and implications for the results obtained in this lab.

RESULTS

Examples of key results for the lab write up are provided below. Contact angle measurements from photos are illustrated in Fig. 6a. Similarly, measurements for the pendant drop method are sketched in Fig. 6b and recorded in Table 1. The calculation of interfacial tension from these measurements proceeds as follows:

$$S = \frac{D_s}{D_e} = \frac{0.942 \text{ mm}}{2.54 \text{ mm}} = 0.371 \quad (4)$$

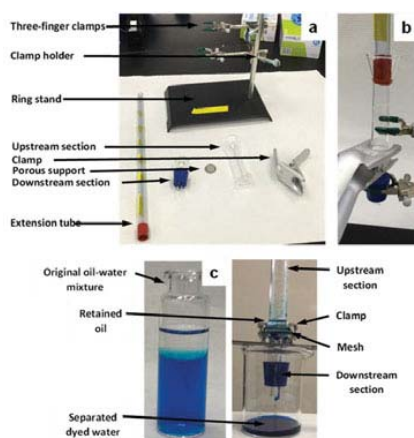


Figure 5. Oil-water separation and breaking height experiment. (a) Flow cell components. (b) Extension tube attachment. (c) Flow cell assembly and oil-water separation experiment.

$$\frac{\gamma_{ow}}{(\rho_w - \rho_o)gD_c^2} = 4.159 \quad (5)$$

The oil used in this example is tetradecane, for which $\rho_o = 0.7596 \text{ g/cm}^3$.

$$4.159 = \frac{\gamma_{ow}}{(997 - 759.6) \text{ kg/m}^3 (9.81 \text{ m/s}^2) (0.00254 \text{ m})^2} \quad (6)$$

where

$$\gamma_{ow} = 62.5 \text{ mN/m}$$

The breakthrough height measurements and predictions are summarized in Fig. 6c and Table 2.

Table 1: Measured lengths from pendant droplet photo.

Parameter	Measured on photo	Actual length
D_t	29 mm	0.635 mm
D_c	116 mm	$(116 \text{ mm} / 29 \text{ mm} \times 0.635 \text{ mm}) = 2.54 \text{ mm}$
D_s	43 mm	$(43 \text{ mm} / 29 \text{ mm} \times 0.635 \text{ mm}) = 0.942 \text{ mm}$

Table 2: Predicted and measured breakthrough pressure.

P_{break} for 150 wire/inch mesh	
Measured	1.15 kPa
Predicted	0.98 kPa

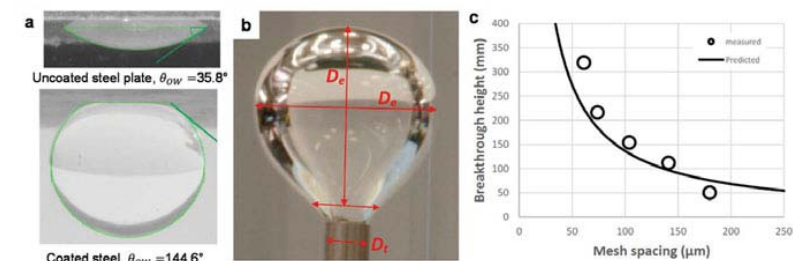


Figure 6. Example results. (a, b) Processed contact angle measurement (a) and pendant drop method (b) photos. (c) Example of measured variation of breakthrough height vs. mesh spacing (symbols) compared to theory (solid line).

CONCLUSION

In the laboratory module presented here, students produce a superoleophobic membrane and use it to separate an oil-water mixture. Through a combination of fabrication, visualization, and measurement of a simple device, students directly observe how structuring on the nanoscale can significantly alter material properties. Furthermore, this module provides students with a clear example of how such properties can be exploited in a practical device. The relevance of nanotechnology to mechanical engineering is highlighted by experiments designed to connect with concepts from fluid mechanics and to show applications in petrochemical processes.

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