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Thermodynamics of Wettability: A Physical Chemistry Laboratory Experiment

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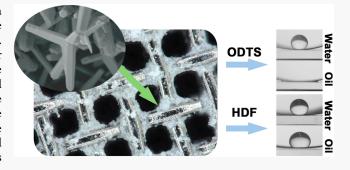
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ABSTRACT: In this laboratory experiment, students modify a series of surfaces and explore the effects of varying surface chemistry and texture on wettability by different probe liquids. Students begin by building a simple contact angle goniometer utilizing their mobile phone cameras. Next, they contrast the wettability of planar glass substrates functionalized with alkyl silanes and fluorinated alkyl silanes and calculate surface free energies using Owens/Wendt plots. Subsequently, they synthesize ZnO tetrapods as robust textural elements and spray deposit the tetrapods onto stainless steel meshes to develop hierarchical texturation, which upon subsequent surface functionalization yields superhydrophobic and oleophobic surfaces. The series of experi-



ments allow them to investigate the manner in which textured surfaces deviate from Young's equation and provide a vivid illustration of the thermodynamics of surface wettability. The laboratory exercise further provides a striking visual analogy for illustrating free energy landscapes and serves as a tangible means to demonstrate the role of surface chemistry with regards to the midstream oil-transportation infrastructure.

KEYWORDS: Wettability, Superhydrophobic, Energy Landscapes, Surface Free Energy, Metastability, Contact Angles, Upper-Division Undergraduate, Physical Chemistry, Hands-On Learning, Manipulatives, Surface Science

■ INTRODUCTION

Investigations of wettability provide a strikingly visual means of illustrating subtle differences in intermolecular interactions at macroscopic scales. Understanding of the fundamental aspects of wettability has evolved substantially over the years; mathematical models describing the thermodynamics of wettability for surfaces are well-documented in the surface chemistry literature. 1,2 This progression in understanding has been crucial to enabling the design of surfaces that facilitate passive separation of oil-water emulsions based on orthogonal wettability,³⁻⁵ enable safer handling of viscous liquids,⁶⁻⁸ and underpin antifogging, 9,10 as well as anti-icing applications. 11,12 The interactions of liquid droplets with (textured) surfaces also allow for illustration of concepts such as sampling of free energy landscapes, which represents a fundamental tenet in understanding of chemical reaction trajectories, protein conformations, and solid-state polymorphism. 13-15

Young's equation (eq 1), developed in 1805, described wettability by relating contact angle measurements, the angle between the solid–liquid interface and the liquid–vapor interface for a drop of liquid placed on a surface, to the balance of interfacial forces between the solid, liquid, and vapor interfaces. ^{16,17} In eq 1, γ_s , γ_{sl} , and γ_l represent the surface free energy of the solid–vapor, solid–liquid, and liquid–vapor

interfaces, respectively, and $\boldsymbol{\theta}$ represents the measured contact angle.

$$\gamma_{\rm s} = \gamma_{\rm sl} + \gamma_{\rm l} \cos \theta \tag{1}$$

This was followed by differentiation of Cassie—Baxter and Wenzel wetting regimes, which accommodated roughness as a contributing factor in 1944 and 1936, respectively. More recently, as advancements in technology have enabled precise control in design of nanotextured surfaces, constitutive equations have been rigorously re-evaluated as they fail to describe more complex interactions, such as the internal Laplace pressure. This has led to the development of proposed modifications to the Cassie—Baxter equation and to the inclusion of re-entrant curvature as a geometric factor underpinning the design of some of the lowest energy surfaces ever known. 1,21

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From these works, several key design principles have become apparent. The nature of the chemical moieties exposed on a surface plays a key role in determining the inherent wettability of a surface. Presentation of higher energy functional groups, with stronger intermolecular interactions, yields a surface with a greater proclivity to be wetted by various liquids. In contrast, presentation of lower energy functional groups leads to a weaker interaction. The surface tension of the probe liquid then determines its general affinity toward surfaces in comparison to other liquids. The stronger the cohesive interactions of a probe liquid, the more likely it is to remain beaded up on a surface rather than interact with a surface via wetting. As such, the balance of cohesive and adhesive interactions results in stronger or weaker surface/liquid interactions, which are manifested as lower or higher contact angles, respectively. In general, surfaces that have a water contact angle greater than or less than 90° are considered to be hydrophobic or hydrophilic, respectively. Similarly, surfaces with an oil contact angle greater than or less than 90° are considered to be oleophobic or oleophilic.²² By altering the proportion of a surface that interacts with an impinging liquid droplet, geometric texturation of the surface can accentuate, or more rigorously, modulate, the inherent wettability of a surface. For example, surface chemistries that are hydrophobic on flat surfaces, yield superhydrophobic surfaces with contact angles above 150° when applied to textured surfaces. Conversely, surfaces that are hydrophilic often become superhydrophilic as a result of texturation, often manifested in the "flash spreading" of droplets across the surface.²³ Fabrication of superoleophobic surfaces is most challenging given the weak cohesive interactions between hydrocarbon molecules; however, surfaces with a combination of low surface energy or specific texturation features characteristic of reentrant curvature have been shown to produce surfaces that are not wetted by oil.^{24,25}

While the above-mentioned models describe the balance of forces as a liquid droplet impinges on a surface, a solid's surface free energy is not readily accessible from contact angle measurements because both are unknown, and the value of $\gamma_{\rm sl}$ is dependent on the liquid and solid under consideration. A number of models that enable determination of the surface free energy of a solid have been described.²⁶ The Zisman method determines a quantity designated as the critical surface free energy, which is distinct from γ_{st} and is defined as the surface tension of a liquid needed to completely wet a given surface. The method provided an excellent starting place to quantitatively compare surface energies but is only valid when evaluating lower energy surfaces that exhibit only dispersive interactions. The Owens/Wendt method is more broadly applicable. The method builds on Fowkes' method, which partitioned surface free energy into the sum of components representing various interactions, including dispersion, polar, hydrogen, induction, and acid-base contributions. Owens and Wendt combined all nondispersive components into a singular polar interaction component. Measurement of contact angles with at least one probe liquid with negligible polar interactions and one probe liquid with negligible dispersive interactions allows for the surface free energy of the solid, γ_s to be inferred using the linearized form of the Owens/Wendt equation, eq 2. The superscripts d and p represent the dispersive and polar components, respectively.²

$$\frac{\gamma_{l}(1+\cos\theta)/2\sqrt{\gamma_{l}^{P}}}{y} = \frac{\sqrt{\gamma_{s}^{d}}\sqrt{\frac{\gamma_{l}^{d}}{\gamma_{l}^{P}}}}{m} + \frac{\sqrt{\gamma_{s}^{P}}}{b}$$
(2)

A number of laboratory experiments and demonstrations exploring concepts of wettability have been developed. 28,29,38,39,30-37 Experiments that allow students to investigate the wettability of naturally low energy surfaces, such as the lotus leaf, have been designed. These demonstrate the effects of surface texturation and illustrate the role of epicuticular waxes in modifying the surface chemistry. Other experiments have used replica molding to allow students to create biomimetic, superhydrophobic surfaces using naturally textured surfaces as templates. 30,32 Experiments utilizing commonly found patterned objects such as the surfaces of recordable compact disks (CD-R) have also been described. 31,32 Further laboratory exercises have utilized carbon soot, 33 methyltrichlorosilane, 34 TiO2 nanoparticles, 35,36 and electroless deposited copper particles³⁷ to provide texturation. For instance, Kabza and co-workers designed a laboratory exercise that enabled students to calculate the critical surface energy of readily available materials such as glass and polytetrafluoroethylene (PTFE) using Zisman plots.³⁸ In addition, several goniometer designs have been reported that provide facile access to studies of wettability within teaching laboratories and are, furthermore, conducive to home assembly and remote instruction. 40-42

The upper-level laboratory exercise described, herein, combines learning objectives from previously designed experiments to provide a comprehensive view of the design of surfaces with controlled wettability. Students work to build a contact angle goniometer to measure contact angles and initially to functionalize planar surfaces with alkyl silanes to explore effects of modifying surface chemistry. Images are processed using a Contact Angle plugin for ImageJ. These surfaces would be expected to generally follow Young's equation, as the surface energy should have minimal contributions arising from texturation effects. Students construct an Owens/Wendt plot to determine the surface free energy of each of the samples based on contact angles measured using a series of four probe liquids with varying surface tensions.

Students also synthesize ZnO nanotetrapods as robust textural elements and then spray coat them onto stainless steel mesh surfaces. The choice of the tetrapod geometry is particularly opportune since these structures are deposited on surfaces with at least one or more protuberant arms and cannot be close packed, yielding a reliable means of defining 3D texturation at macroscopic scales without need for lithographic patterning. These surfaces demonstrate texture at multiple scales, which can be visualized by scanning electron microscopy (SEM) or through use of a digital or optical microscope. They can be further functionalized with the alkyl silanes to produce surfaces with surface chemistry analogous to the planar surfaces prepared on glass. By beginning with evaluation of simpler, planar systems students can decouple the effects of surface chemistry and the surface tension of probe liquids. By creating textured surfaces functionalized with the same alkyl silanes as used for the glass surfaces, they can then build on this understanding to evaluate the effects of surface texture and explore additional theories, such as the Cassie-Baxter and Wenzel wetting regimes with direct parallels to metastable and equilibrium positions on free energy landscapes. Figure 1 shows an overview of the design process students perform to generate surfaces with controlled

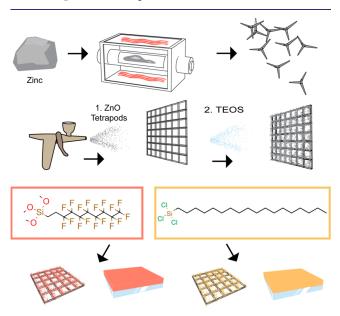


Figure 1. Overview of the design of surfaces with controlled wettability showing ZnO tetrapods generated by thermal treatment of zinc metal in a tube furnace. ZnO tetrapods and TEOS are sprayed onto stainless steel mesh surfaces and functionalized with ODTS or HDF. These are compared to glass surfaces functionalized with ODTS and HDF.

wettability in this laboratory experiment. The complete laboratory module is included as Supporting Information.

The experiment builds on our previous works, wherein ZnO nanotetrapod-based membranes and coatings were developed to enable handling and transportation of viscous oils—such materials play an increasingly important role in midstream transportation of bitumen across the railcar, pipeline, shipping arteries that transport fuel across North America.² Specifically, superoleophobic coatings allow viscous oil to glide out of containers used during transport of bitumen, thereby reducing maintenance costs, decreasing downtime, alleviating the need for thermal jacketing required to flow rheologically challenging fluids, enhancing product recovery, and mitigating the need to dilute viscous oil with light hydrocarbons. 3,5,8 Translation of industrial research to the teaching lab, overlooking the train tracks where railcars carry bitumen from Northern Alberta to Houston Gulf Coast refineries provides a tangible means to place chemistry in context. The exercise provides students interested in pursuing career paths involving research with a broad overview of key concepts in thermodynamics and surface chemistry, while directly linking to an application of chemistry at massive scales. The topic of research further dovetails with broader discussions of the energy infrastructure and the distinctive challenges of the energy transition with regards to hard-to-abate sectors. Table 1 provides an overview of the learning objectives for this laboratory experiment as well as a series of accompanying checkpoints that allow for assessment of whether learning objectives were met. Student reports from a recent semester were reviewed to determine whether students demonstrated understanding of key concepts in the learning objectives. Results from this assessment are detailed throughout the Experimental Overview section. Oral reports

Table 1. Learning Objectives and Key Assessment Points

Students will consider applications of materials design in addressing real-world Applications of coatings and membranes designed with controlled wettability in the midstream Student laboratory report introductions oil and gas industry are introduced within the laboratory manual. Students are encouraged to introduce applications of coatings/membranes with controlled wettability and include references in their reports.	earn a variety of laboratory skills and use the observations they The laboratory manual provides graphics and decisions and adjust their design techniques. Teaching assistants serve as checkpoints in discussing the practical aspects of materials design, such as those employed during spray coating and during nuances of design by checking functionality of the goniometer. Goniometer and the quality of a coating prepared in low-stakes "practice runs".	raw connections between fundamental concepts in thermody- and processing and analysis/questions and oral ding force balance, free energy landscapes, and metastability to can trace the progression of mathematical models that describe wettability. exam questions exam questions exam questions exam questions hermodels capable of describing complex hermomena.	e able to systematically predict trends in materials Prior to performing the lab, students predict contact angles for each of the surfaces they plan to Lab manual pre-lab questions and data processing and seed on the chemical and physical elements of coating design. a series of questions which guide them to distinguish effects of probe liquids, surface chemistry, and texturation.	Learning Objective Activity Checkpoint
		S	By decoupling effects of surface chemistry, texturation, and probe liquid surface tension, students landscapes, and metastability to can trace the progression of mathematical models that describe wettability. The laboratory manual provides graphics and adjust their design techniques. Practical aspects of materials design of the goniometer. The laboratory manual provides graphics and adjust their design in addressing real-world Applications of coatings/membranes with controlled wettability and include references in their reports.	Students will be able to systematically and critically predict trends in materials prior to performing the lab, students will be able to systematically and critically predict trends in materials properties based on the chemical and physical elements of coating design. Students will draw connections between fundamental concepts in thermody- macroscale phenomena. Students will draw connections between fundamental concepts in thermody- macroscale phenomena. Students will cam a variety of laboratory skills and use the observations they practical aspects of materials design in addressing real-world and physical elements of coating design. The laboratory manual provides graphics and descriptions of mathematical models that describe wettability in the midstream a variety of laboratory skills and use the observations of materials design in addressing real-world and adjust their design in addressing real-world and physical elements of coatings/membranes designed with controlled wettability in our energy infrastructure. Lab manual pre-lab questions and data processing and data processing and analysis/questions and data processing and analysis/questions and adjust their design that descriptions that descriptions that descriptions that descriptions that guide students to consider a variety of laboratory manual provides graphics and descriptions that descriptions and descriptions of outlings and membranes design, such as those employed during spray coating and during propagated in low-stakes "practice runs". Students will be an avariety of laboratory report introductions of outlings may be a coating prepared in low-stakes "practice runs". Students while the processing and advantage and descriptions of coatings/membranes design and the quality of a coat
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and responses to prelaboratory questions were assessed by the teaching assistant.

EXPERIMENTAL OVERVIEW

The experiment was designed in 2017 and has been performed by students in the upper-level physical chemistry lab over the course of eight semesters resulting in over 300 students having completed the experiment and allowing for the feedback of students to iteratively improve the experiment each semester. Students work in groups of three to four rotating to new experiments within the lab after 2 weeks with 3 h laboratory periods, allowing for a total of 6 h to complete this experiment. Each experiment taught within the lab has a different teaching assistant who prepares materials for the laboratory and provides guidance to the students in performing the experiments.

In the first week of the exercise, students functionalize glass slides with octadecyltrichlorosilane (ODTS) and (heptadeca-fluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane (HDF) silane-based monolayers, construct a contact angle goniometer, and measure contact angles for the coatings they have prepared. This ensures that by the end of the first week students have collected all data necessary to evaluate the planar surfaces and are able to generate Owens/Wendt plots to assess surface energy. Structures of ODTS and HDF in the presence of a schematic of a glass surface are shown in Figure 2A. An image of a typical goniometer constructed by students (Figure 2B), example contact angle images produced using a cell phone (Figure 2C–E), and an example Owens/Wendt plot produced from data collected in the lab (Figure 2F) are additionally shown in Figure 2. In the first week, students additionally

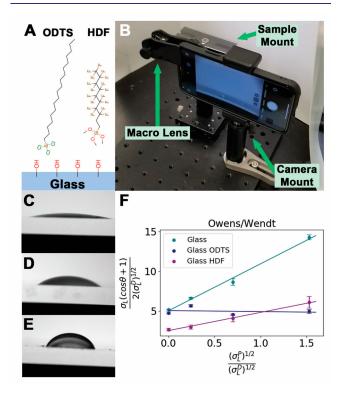


Figure 2. (A) Structures of HDF and ODTS used to functionalize surfaces. (B) Contact angle goniometer built by students. (C-E) Typical contact angle images collected using a mobile phone. (F) Owens/Wendt plot for surfaces prepared on glass.

synthesize ZnO nanotetrapods, spray-coat stainless steel substrates with the ZnO nanotetrapods and tetraethylorthosilicate. The tetraethylorthosilicate layer is added to enhance adhesion of the ZnO to the stainless steel surfaces. In the second week, students apply the silane-based monolayers (ODTS and HDF) to the ZnO-coated stainless steel meshes and measure the contact angles for those coatings. Figure 3A and B shows SEM images of typical ZnO nanotetrapods produced by students as well as optical images of a ZnO functionalized stainless steel mesh obtained via image stacking to show resulting surface texturation.

A detailed lab manual and instructor notes are provided as Supporting Information. Instructional videos for making a steel boat, setting up the quartz tube in a furnace, and spray coating are posted online, https://youtube.com/playlist?list=PLxOi8aEvgwUTUvbcGwI-bIN88eAJHsPKz.

Prior to performing the laboratory exercise, students complete prelab questions designed to encourage them to make predictions regarding the wettability of the various surfaces based on background information presented within the laboratory manual. They also verify their ability to use ImageJ freeware, so that any technical issues that may arise can be worked out with teaching assistants within the first laboratory period. Between the first and second laboratory, students are tasked with determining contact angles for each of the planar surfaces prepared on glass and to construct their Owens/Wendt plots. This provides an opportunity for students to discuss their results and, if they find that any of their photographs were difficult to interpret, inculcates troubleshooting skills related to experimental replicates, instrument building, and software use.

Students initially built a contact angle goniometer similar to that described by Lamour and co-workers.⁴⁰ Students are less familiar with using digital cameras, and based on feedback we modified the apparatus to utilize a simple cell phone camera mounted with an inexpensive clip-on macro lens attachment as shown in Figure 2B. Students who performed the exercise observed reasonable trends in contact angles as shown in example data presented in Figure 4 and Table 2.

The laboratory manual presents a list of prompts that guides students to systematically evaluate their data trends. Students were asked to first compare the effect of using different probe liquids on contact angle. Clear trends were consistently observed demonstrating a decrease in contact angle with decreasing surface tension of the probe liquid going from water to formamide, soybean oil, and then n-hexadecane. This follows expected trends where higher surface tension liquids, which have stronger cohesive interactions, should more readily bead up on surfaces, whereas lower surface tension liquids, with weaker cohesive interactions, more readily interact with surfaces and therefore have generally lower contact angles. Student laboratory reports from a recent semester were reassessed to determine whether students demonstrated an ability to systematically predict trends in materials properties as described in the first learning objective listed in Table 1. Nine of ten groups demonstrated an understanding of this distinct role the probe liquid surface tension plays in determining wettability. The students were then asked to compare wettability across the flat surfaces prepared on glass. Students again consistently observed an increase in contact angle going from a cleaned glass surface to a silanefunctionalized surface and could observe that functionalization with fluorinated silanes yielded contact angles that remained

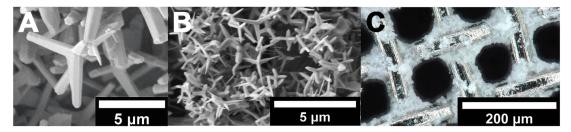


Figure 3. (A, B) SEM images of ZnO nanotetrapods. (C) Image of 3D ZnO nanotetrapods arrayed on stainless steel mesh taken via image stacking digital microscope images.

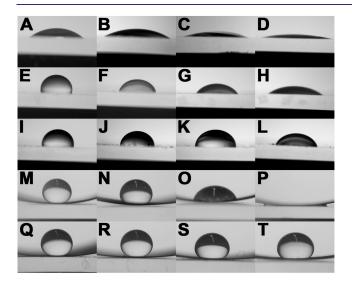


Figure 4. Contact angles for (A–D) glass, (E–H) glass + ODTS, (I–L) glass + HDF, (M–P) stainless steel mesh + TEOS + ODTS, and (Q–T) stainless steel mesh + TEOS + HDF acquired using (A, E, I, M, Q) water, (B, F, J, N, R) formamide, (C, G, K, O, S) soybean oil, and (D, H, L, P, T) *n*-hexadecane as probe liquids.

higher when moving to lower surface tension liquids. This follows anticipated trends where functionalization with alkyl silanes and fluorinated alkyl silanes lowers the surface free energy. For alkyl silanes, the presentation of nonpolar alkyl chains at the surface provides only weak van der Waals interactions with the polar probe liquids. The cohesive interactions within the high surface tension probe liquids are stronger and the liquid maximizes cohesive interactions by beading up, producing higher contact angles. For the alkylterminated silanes, as less polar probe liquids with lower surface tension are used, the cohesive forces within the liquid become more similar to the adhesive forces between the surface and the liquid, so the droplet spreads more readily.

As C-F bonds represent the strongest known organic covalent bond with a bond energy of 105.4 kcal/mol, it would be reasonable to anticipate that C-F dipole moments would

result in stronger binding with a polar water molecule. 43,44 However, when comparing the wettability of fluorinated versus nonfluorinated alkyl terminated surfaces, differences in size play a significant role. The difference in the van der Waals radius of hydrogen versus fluorine is around 1.2 versus 1.47 Å, respectively, and the difference in the van der Waals diameter of an alkyl chain is around 4.2 Å versus around 5.6 Å for a perfluorinated chain.⁴⁴ These differences in size are significant enough to affect factors such as the packing density of the selfassembled monolayers and the rigidity of the carbon chains. Dalvi and Rossky calculated differences in water solvation free energy for hydrocarbons versus perfluorinated alkyl chains using all-atom molecular dynamics simulations in which a hydrocarbon was transformed into a perfluorinated hydrocarbon in five stages to distinguish the effects of changes made at each stage. 43 These authors determined that the "fattening" step, which involved changing the Lennard—Jones diameter resulted in the most significant changes in solvation free energy. Thus, it is often observed that fluorinated surfaces demonstrate higher contact angles under analogous conditions than those functionalized with nonfluorinated alkyl chains. These differences in resulting surface energy can be subtle, on the order of around ten degrees, and were difficult to observe within the laboratory exercise.⁴⁴

When considering differences in wettability toward non-polar, lower surface-tension-probe liquids between surfaces functionalized with nonfluorinated versus fluorinated alkyl chains, differences were easily observed. While it can be anticipated that both surfaces exhibit solely dispersive interactions with the nonpolar probe liquids, key differences in wettability have again been attributed to differences in the size of fluorine versus hydrogen and the resulting differences in packing density. As less densely packed surfaces, fluorinated surfaces exhibit generally weaker dispersive interactions compared to hydrocarbon-functionalized surfaces. Thus, the overall weaker adhesive interactions in fluorinated surfaces results in generally higher contact angles compared to the hydrocarbon-functionalized surface.

Students prepared Owens/Wendt plots, similar to that shown in Figure 2 F for the flat surfaces. They were able to

Table 2. Contact Angles for Prepared Surfaces for Each Probe Liquid

	Probe Liquid				
Surface	Water	Formamide	Soybean Oil	n-Hexadecane	Surface Energy (mN/m)
Glass	33.7 ± 4.2	28.9 ± 11.0	24.8 ± 4.6	11.3 ± 1.7	60.4
Glass ODTS	111.3 ± 1.9	91.0 ± 1.1	50.7 ± 3.2	35.1 ± 4.6	19.8
Glass HDF	102.6 ± 5.5	97.0 ± 5.2	97.7 ± 4.3	88.8 ± 3.7	12.0
Stainless Steel Mesh ZnO ODTS	151.1 ± 4.3	132.1 ± 8.7	70.2 ± 3.0	0 ± 0	n/a
Stainless Steel Mesh ZnO HDF	151.4 ± 0.9	151.4 ± 2.6	132.7 ± 7.1	128.6 ± 3.5	n/a

calculate the surface energy of the prepared flat surfaces after fitting the data for each surface with a linear regression following eq 2. Values obtained were concordant with those found in the literature. In the example data presented the surface energy of glass, glass with ODTS, and glass with HDF was found to be 60.4, 19.8, and 12.0 mN/m, respectively.

Students could then compare these trends to contact angles collected on the ZnO nanotetrapod textured stainless steel meshes. Both the ODTS and the HDF-functionalized surfaces were typically found to be superhydrophobic, as anticipated given the lowered surface free energy of alkyl silane and fluorinated alkyl silane functionalized surfaces combined with an enhancement in this inherent wettability upon texturation of the surface with ZnO tetrapods. Students are asked to be careful during the spray coating process to ensure that a uniform layer of ZnO tetrapods was deposited. Tips to ensure success are presented within the Supporting Information and spurred discussion of challenges of chemical manufacturing at scale. The ZnO-functionalized surface coated with ODTS went from being superhydrophobic to superoleophilic as the surface tension of the probe liquids decreased. However, the ZnOfunctionalized surface coated with HDF maintained high contact angles demonstrating superhydrophobicity and oleophobicity. Here, the effects distinguishing the wettability of fluorinated and nonfluorinated surfaces are exacerbated, allowing students to observe clear differences. As discussed above, when exposed to nonpolar probe liquids, fluorinated surfaces exhibit weaker dispersion interactions compared to the nonfluorinated organosilane-functionalized surfaces. Therefore, whereas the ODTS-functionalized surface is more easily wetted by nonpolar probe liquids, the HDF-functionalized surface still repels even the lowest surface tension probe liquids.

When reviewing student reports, eight of ten reports included correct descriptions of the effects of texturation on wettability. Students were then able to discuss why they could not use the Owens/Wendt plot to evaluate surface energies for the textured surface and were encouraged to consider plastron formation and the role of geometric effects. Student laboratory reports were further assessed to evaluate the extent to which students demonstrated an ability to draw connections between concepts in thermodynamics, such as force balance, and ideas, such as metastability to the construction of mathematical expressions capable of describing macroscale phenomenon, as described in the second learning objective in Table 1. Nine of the ten reports reviewed gave detailed descriptions describing the balance of forces described within Young's equation and further described how the model fails to describe wettability of textured surfaces. Each further described how the Cassie-Baxter and Wenzel wetting regimes can be used to alter Young's equation to more effectively describe wettability in cases where the surface under consideration is textured. Student reports were further assessed to determine whether students demonstrated the ability to effectively prepare manuscripts as described in the last learning objective listed in Table 1. Within the ten reports assessed, students generally demonstrated an understanding of the structure of scientific manuscripts. There were only a couple of instances where the contents of a section would have been more suitable in a different section of the manuscript. Additionally, the manuscripts demonstrated few instances where typical style guidelines were not followed. This is not altogether surprising since students begin formatting lab reports following ACS guidelines in their first year and, thus, have had extensive prior

exposure to the process. Similarly, all student groups were able to effectively describe the real-world applications of the coatings. Assessment of whether students demonstrated an ability to use their observations to adapt their laboratory techniques when performing more nuanced tasks, such as spray coating, as described in the third learning objective listed in Table 1, is somewhat subjective. Teaching assistants who taught the lab in different semesters were asked to comment on the extent to which they felt students achieved this learning objective. An illustrative response is:

I saw most of the students got better at spray-coating as they practiced. The first, practice coating that students made, even after they read the manual, was often quite inhomogeneous and rough. In these cases, we would look at the coating and compared it with some of the best, 'ideal' coating samples and discuss what might have gone wrong, e.g., whether they were not spraying from a far enough distance away, moving too slowly, starting at the wrong point, or having issues with the spray-coater being clogged. Then, the second coating was usually much better, and they saw comparable results to the 'ideal' coating samples. Students similarly quickly learned how to set up the goniometer. Some students were able to set up the goniometer following the manual and successfully got their contact angle pictures without much discussion. Others had some trouble with factors such as focusing, lighting, or adjusting the stage height. However, after comparing their test photos to examples and discussion possible issues they might be having, they were able to troubleshoot to fix the issues and had no issues setting the system up the next week.

Some specialized equipment is required to complete the lab including a tube furnace used to generate the ZnO tetrapods and a spray coater used to apply ZnO tetrapods and tetraethyl orthosilicate to stainless steel meshes. Texturation can additionally be visualized using an optical microscope. If availability of this equipment is limiting, the experiment could be performed by generating just the functionalized glass surfaces to greatly reduce the cost.

HAZARDS

All sample preparation should take place within a chemical fume hood. Personal protective equipment, such as gloves and safety glasses, should always be worn during preparation and handling of samples. Temperatures reached by the tube furnace (950 °C) are extremely hot. The tube should only be handled once the tube furnace has cooled down. Thermal gloves should be worn when opening the tube furnace to increase the cool down rate and no portion of the interior of the tube furnace should be touched during this process. Edges of stainless steel meshes can be quite sharp. Cut-resistant gloves may be worn while working with the stainless steel meshes. Tetraethylorthosilicate is a flammable liquid, has acute toxicity, is an eye irritant, and is harmful if inhaled. Octadecyltrichlorosilane is corrosive and heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane is an irritant. Toluene is highly flammable, toxic, an irritant, and a suspected teratogen. 1-Butanol is flammable, corrosive, and an irritant. Ammonium hydroxide is corrosive and an irritant. Formamide is a suspected carcinogen and teratogen. Glycerol may serve as a reasonable substitute for use of formamide. Safety datasheets for all chemicals utilized should additionally be reviewed, and solids and liquids should be disposed of as hazardous waste. Given that only a small quantity of many of the chemicals is

required, providing students with the minimum quantity required is beneficial.

SUMMARY

Students were able to successfully functionalized glass slides with alkylsilanes, build a contact angle goniometer using their cell phones as cameras, and measure contact angles using a series of probe liquids. Analysis of contact angles using a Contact Angle plugin for ImageJ allowed for generation of Owens/Wendt plots. Values of surface energy obtained by students were comparable to literature values. Students additionally generated superhydrophobic and oleophobic coatings through spray coating ZnO nanotetrapods, which they synthesized, onto stainless steel meshes and functionalizing them with alkylsilanes. The laboratory successfully enables exploration of concepts of cohesive and adhesive forces, Young's equation, surface free energy, Cassie—Baxter and Wenzel wetting regimes, and design of surfaces with controlled wettability through hands-on experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.2c00243.

Laboratory manual, which provides background information given to students, prelaboratory questions, detailed instructions on performing the experiments, questions to guide report writing, oral exam questions, and instructions for use of ImageJ, and instructors notes, which provides a detailed list of materials required to complete the lab and additional notes on preparation to perform the lab and cleanup (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

Instructional videos for making a steel boat, setting up the quartz tube in a furnace, and spray coating are posted online, https://youtube.com/playlist?list=PLxOi8aEvgwUTUvbcGwIbIN88eAJHsPKz.

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