Bouncing droplets: A Hands-on Activity to Demonstrate the Properties and Applications of Superhydrophobic Surface Coatings

Carolina Cionti†, Tommaso Taroni†, Daniela Meroni*

[1] Department of Chemistry, Università degli Studi di Milano, via Golgi 19, 21033 Milan, Italy

[2] INSTM (Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali), Via Giusti 9, 50121 Florence, Italy

† These authors equally contributed to the work

* Corresponding author

ABSTRACT

Here we report a hands-on activity addressed to Master's students of Physical Chemistry and Materials Science courses on the properties and applications of superhydrophobic surfaces. This simple and intuitive experience can be also proposed to undergraduate and high school students, thanks to its application-oriented approach and tangible results. Superhydrophobicity was achieved by the functionalization of oxide powders with alkylsilanes and their subsequent deposition on a glass substrate. The film superhydrophobicity was assessed by different application tests and compared to the behavior of model hydrophobic, hydrophilic and superhydrophilic surfaces. Anti-stain properties were tested against both model dye solutions and everyday liquids. Films were fouled with graphite and dye powders to compare the self-cleaning capabilities of the different surfaces, while single droplet-transport was achieved adding magnetic particles. This engaging and adaptable experience introduce students to basic concepts of surface science in an intuitive and tangible way.

KEYWORDS

Physical Chemistry, Surface Science, Materials Science, Hands-On Learning/Manipulatives, High School/Introductory Chemistry, First-Year Undergraduate/General, Upper-Division Undergraduate

INTRODUCTION

Very low surface wetting by water, generally called superhydrophobicicty, is a phenomenon often observed in nature, such as in lotus leaves, rose petals, butterfly wings, gecko feet and many other animals and plants.[1] In natural surfaces, superhydrophobicity is achieved via the synergy of multiscale texture and surface chemical composition.[2] Much effort has been devoted to mimicking natural superhydrophobic surfaces owing to the numerous potential applications of materials with controlled wetting properties: self-cleaning and anti-stain materials, liquid-transport and drag-reduction systems, anti-corrosion and anti-icing surfaces, just to name a few.[3] In the last two decades, the field of wetting modification has experienced tremendous breakthroughs both in terms of more accurate mimics of natural materials.[2,4] as well as in the development of surfaces with unprecedented wetting features[5-7]. Drawing inspiration from nature, surfaces with robust self-cleaning superhydrophobicity could be designed[8-9] and, thanks to a firmer theoretical understanding of wetting phenomena, innovative properties could be achieved, such as high adhesive superhydrophobicity[10], anisotropic superhydrophobicity[11], switchable superhydrophobicity[12-13], superomniphobicity[14] and superhydrophobicity from inherently hydrophilic materials[15-16].

Despite the numerous real-life applications and exciting research prospects, surface wetting is often overlooked in Chemistry and Materials Science curricula and even more rarely Bachelor's and Master's students take part in laboratory activities providing a direct approach to these concepts. Filling this gap is crucial considering that wetting properties are an ideal topic to demonstrate basic concepts of surface science in an intuitive and tangible way.

While the literature offers a few laboratory activities on surface wetting modification[17-22], most of them deal with simple hydrophilic/hydrophobic surfaces. Only very few reports offer laboratory activities presenting the preparation of superhydrophobic surfaces.[23-25] However, these experiences require long waiting times (from several hours to 2 days) and the preparation and characterization steps often require uncommon equipment for teaching laboratories, like UV/ozone cleaners or spin coaters, and expensive instrumentation, such as contact angle measurement instruments and electron microscopes.

Here, we propose a simple and fast hands-on activity for the preparation of superhydrophobic coatings based on the deposition of surface functionalized oxide powders. Much emphasis is given to the observation of the superhydrophobic coating properties, highlighting the potential applications in everyday life: from rolling-off and bouncing droplets, to liquid transport capabilities, self-cleaning and anti-stain features.

EXPERIMENTAL OVERVIEW

Wetting describes the interface phenomena occurring between a solid and a liquid and it is usually expressed in terms of contact angle, θ. A first description of the contact angle of a liquid droplet on a solid surface was given by Young in 1805,[26] who related wetting to the liquid surface tension and solid surface free energy. Young's theoretical model referred to ideally flat and homogeneous surfaces (Figure 1A), hence it did not suit well real solids, which are characterized by surface roughness and composition heterogeneity. As a matter of fact, surface texture has a crucial role on the wetting properties of real surfaces. Two theoretical interpretations of the solid-liquid interaction that explicitly take into account surface roughness, were later proposed by Wenzel[27] and Cassie and Baxter[28]. Wenzel model assumes that, when a droplet comes into contact with a rough surface, the solid-liquid contact line follows the material topological variations (Figure 1B). Therefore, in accordance with this model, surface roughness increases the solid-liquid interface and hence enhances the natural wetting properties of the material: rough hydrophilic surfaces become more hydrophilic than their flat counterparts, whereas hydrophobic ones show increased hydrophobicity. However, when it comes to hydrophobic systems with a high degree of surface roughness and, in particular, solids where micro and nanoscale textures coexist (such as micrometric bumps covered by nanostructures, as in lotus leaves), a high degree of water repellency is observed. The so called superhydrophobic behavior, characterized by water contact angles higher than 150° and very low contact angle hysteresis (*i.e.*, low adhesive behavior), cannot be explained by the Wenzel theory. When a hydrophobic surface becomes very rough, the liquid does not follow the material profile as hydrophobic materials have a higher surface energy wet than dry; conversely, the droplet will trap air pockets inside the solid texture and, in this way, the drop will sit on a composite of solid and air (Figure 1C), a behavior called a Cassie-Baxter state. As the liquid contacts the solid only at the top of the surface asperities, droplets in a Cassie-Baxter state show very limited interaction with the solid and hence very low adhesion (non-sticking drops); this behavior is responsible for the self-cleaning and anti-stain properties of superhydrophobic surfaces[29-30].

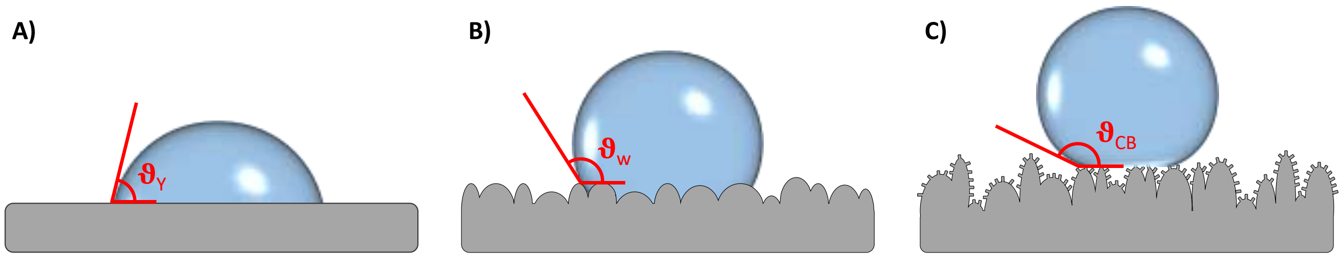

Figure 1. Wetting of a solid surface by a liquid droplet: (A) Young (B) Wenzel and (C) Cassie-Baxter models.

Even though current theoretical understanding has moved past these classical models[31], surface texture has been confirmed to be the most crucial parameter imparting superhydrophobicity. Countless strategies to produce superhydrophobic coatings have been proposed, differing for the adopted materials and strategies for surface texture tailoring. In our activity, metal oxide powders are employed to provide a multiscale surface roughness[32]; their intrinsically hydrophilic surface, due to the presence of hydroxyl groups, is turned into a hydrophobic one by grafting with alkylsilanes, which form stable siloxane bonds with the surface[33-34] (Figure 2). Superhydrophobic coatings can then be easily prepared by depositing the functionalized particles on a substrate (e.g., glass slides, Petri dishes) by a simple drop-casting deposition (Figure 2).

Although different oxides can be used, here we adopted TiO_2 powder, a stable and low-cost material. In this way, this laboratory procedure can be easily integrated with a hands-on activity previously reported by our group on the photocatalytic lithography of superhydrophobic surfaces to achieve superhydrophobic/superhydrophilic wetting contrast.[25]

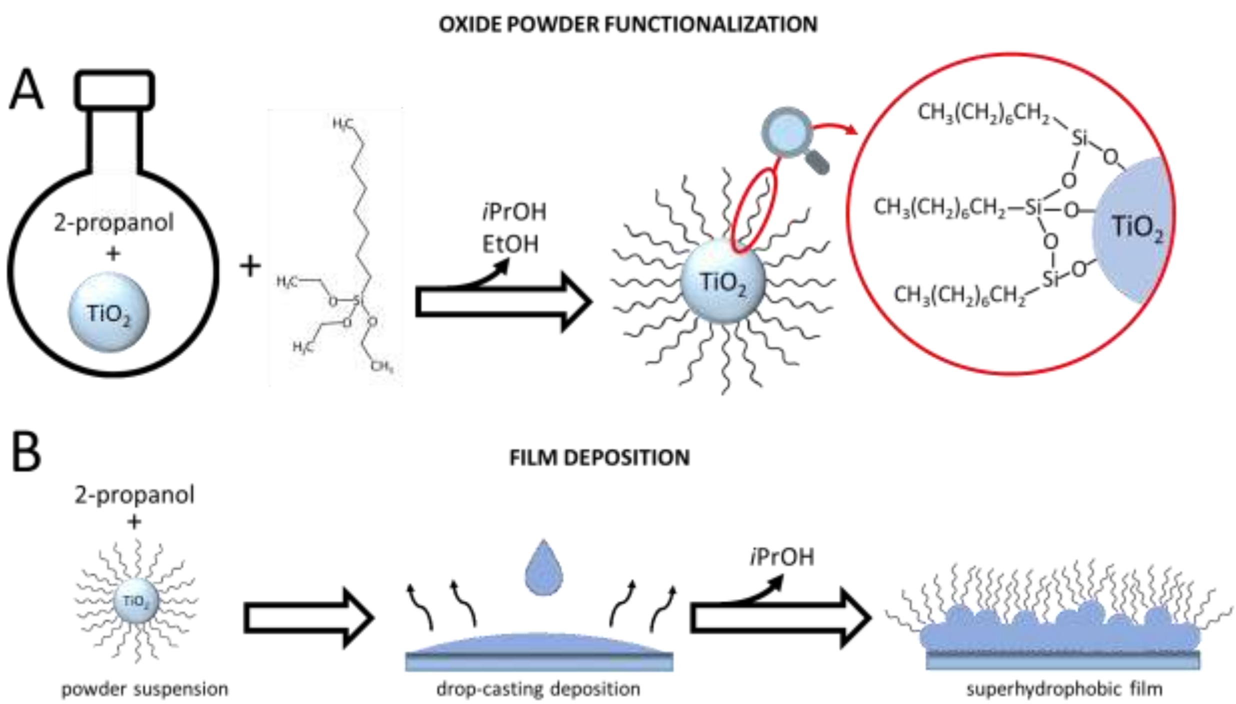

Figure 2. Schematic representation of the superhydrophobic coating preparation: hydrophobic nanoparticles were prepared by impregnating commercial anatase particles with triethoxy(octyl)silane (A); said particles were then deposited by drop-casting a 2-propanol suspension on a glass slide and letting the solvent evaporate, producing a superhydrophobic film (B).

MATERIALS AND INSTRUMENTATION

Anatase titanium (IV) oxide (*ca.* 50 m^2 g^{-1}), triethoxy(octyl)silane, 2-propanol, acetone, methyl orange and PTFE sheets were purchased from Sigma Aldrich; water passed through a MilliQ apparatus was adopted for the preparation of dye solutions. An ultrasonic bath was used for suspension preparation. Surface functionalization was carried out using a rotary evaporator. Superhydrophobic coatings were deposited on soda lime glass slides and glass Petri dishes.

HAZARDS AND SAFETY PRECAUTIONS

Lab coats, safety goggles and gloves should be worn during the activity. Triethoxy(octyl)silane is a skin and eye irritant. Before operating the rotary evaporator, close the safety shield. Film deposition via drop-casting should be performed under fume-hood due to the use of 2-propanol, a volatile and flammable organic solvent.

EXPERIMENTAL PROCEDURE

Functionalization of Oxide Powder with Alkylsilane

In a 100 mL one-neck flask, 0.5 g of oxide was suspended in 50 mL of 2-propanol and then sonicated for 5 min to improve dispersion. Five drops of triethoxy(octyl)silane were added with a Pasteur pipette and the flask was then connected to a rotary evaporator: at ambient pressure, the rotation speed was set to 200 rpm and the bath temperature was progressively increased from room temperature to 50°C within 30 min. At 50°C, the flask was connected to the vacuum line to remove the solvent (approximately 30 min). The dry powders were then collected in a test tube. The successful functionalization of the oxide was assessed by comparing its dispersibility in water with that of the pristine powder.

Drop-casting Deposition of Superhydrophobic Coatings

Substrates (3 glass slides for each group) were cleaned with acetone, rinsed with water, then dried. Functionalized powders were resuspended in 2-propanol (0.05 g in 5 mL) and deposited by drop casting on one of the glass substrates. Solvent was removed by evaporation within a fume hood: the solvent removal can be speeded up by fanning. Reference coatings were prepared by depositing pristine TiO_2 powder on another glass slide according to the same procedure.

Anti-stain Properties

The anti-stain properties of superhydrophobic coatings were tested against different kinds of aqueous solutions, such as dye solutions or wine. The liquid was poured with a Pasteur pipette on the coated substrate, which was kept atilt by placing a glass rod underneath or simply by holding it. As a reference, anti-stain tests were performed also on uncoated glass, PTFE foil and a pristine oxide coated glass slide.

Self-cleaning Features

In order to test the self-cleaning capability of the superhydrophobic coating, graphite powder (prepared by grinding a pencil tip) or other colored powder (*e.g.*, methyl orange) was deposited on the coated glass slide. Then, water was dripped using a Pasteur pipette on the tilted substrate to remove the colored powder with the minimum amount of water. The experiment was repeated on the other provided supports (uncoated glass slide, PTFE foil, and glass coated with pristine oxide) to compare their different behavior.

Liquid Transport Test

A suspension of magnetic particles (iron filings) in water (*ca.* 5 mg mL^{-1}) was prepared. A drop of the magnetic particle suspension was gently deposited on the superhydrophobic coating. The liquid droplet was then moved across the surface, controlled by a small magnet placed under the substrate

RESULTS AND DISCUSSION

Student Experience

The laboratory activity takes 2-3 h, depending on the laboratory expertise of the participants, and was carried out in small groups (4-5 persons). During the waiting time for the oxide functionalization, students prepared the material needed for the application tests (dye solution, magnetic suspension, graphite powder) and familiarized with the drop-casting deposition by preparing a pristine oxide coating on a glass slide. Moreover, they carried out self-cleaning and anti-stain tests on the provided reference surfaces (uncoated glass and PTFE). All the groups were able to successfully carry out the activity and reported their results with photos and videos.

Powder Functionalization and Film Deposition

The oxide powder was functionalized with triethoxy(octyl)silane by reaction between the hydroxyl groups at the TiO_2 surface and the siloxane head-group. The success of the functionalization procedure can be easily determined by a dispersibility test: while pristine oxide powders readily disperse in water medium forming a white slurry due to their hydrophilicity, surface functionalized particles float on the liquid surfaces even after vigorous agitation (Figure 3).

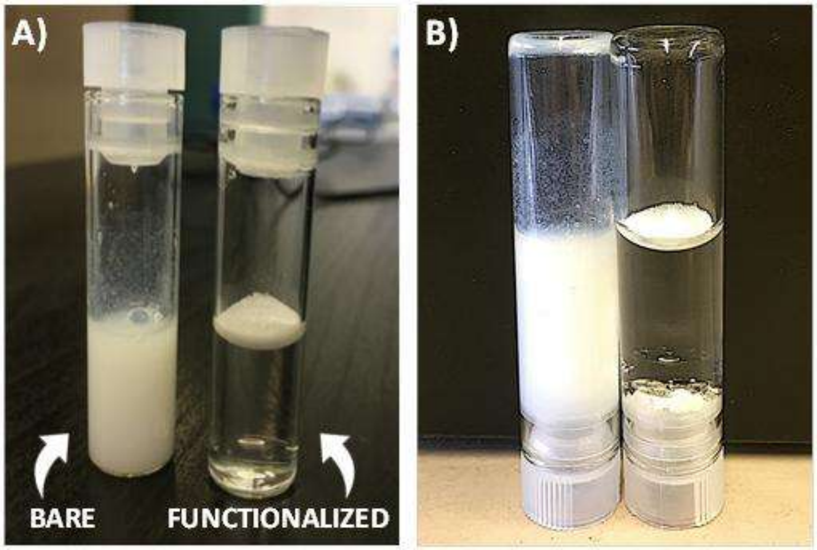

Figure 3. Dispersibility of bare (left vial) and functionalized (right vial) oxide powders (A); flipping or vigorously agitating the vials does not improve the dispersibility of the functionalized particles (B).

Superhydrophobic coatings were prepared by drop casting deposition of the functionalized powder on clean glass slides: this film preparation method is quick, simple and does not require any expensive equipment. The coating roughness imparted by the oxide particles, together with the hydrophobicity of the alkylsilane hydrocarbon chains, gave rise to a Cassie-Baxter behavior of the hybrid coating. Resulting films appeared have low transparency, but showed a relatively good mechanical resistance, as reported in Figure S2.

Application Tests

The superhydrophobic coating properties were tested towards different kinds of applications: self-cleaning, anti-stain and liquid transport tests. For the sake of comparison, tests were always performed also on reference substrates: uncoated glass slides, PTFE foil and pristine oxide films as model surfaces displaying hydrophilic, hydrophobic and superhydrophilic behavior, respectively.

The anti-stain properties of the superhydrophobic coatings were demonstrated by pouring colored aqueous solutions, such as wine or dye solution, on the surface: the liquid droplets were repelled by the surface and rolled off the film without sullying it (Figure 4 A). The contrast with the reference surfaces is sharp, particularly with the uncoated oxide coating, which readily absorbed the dye solution/wine creating large stains (Figure S1).

Moreover, the self-cleaning ability of the functionalized oxide coating was evaluated by covering the surface with graphite or methyl orange powders: by dripping water on the slightly tilted surface, droplets rolling off the surface easily remove dirt particles deposited on it (Figure 4 B and video in the SI). No similar effects can be observed on the reference samples, even on the highly hydrophobic PTFE foil.

Finally, liquid transport tests were performed using a magnetic particle suspension and a magnet: students were able to drive at will a liquid droplet simply by moving the magnet under the film (Figure 4C and video in the SI). The liquid movement can be highlighted by covering the surface with a colored powder (*e.g.*, dye powder as in Figure 4C). With respect to hydrophobic surfaces, liquid transport on superhydrophobic surfaces takes place with no loss of liquid enabling the transport even of very small droplets.

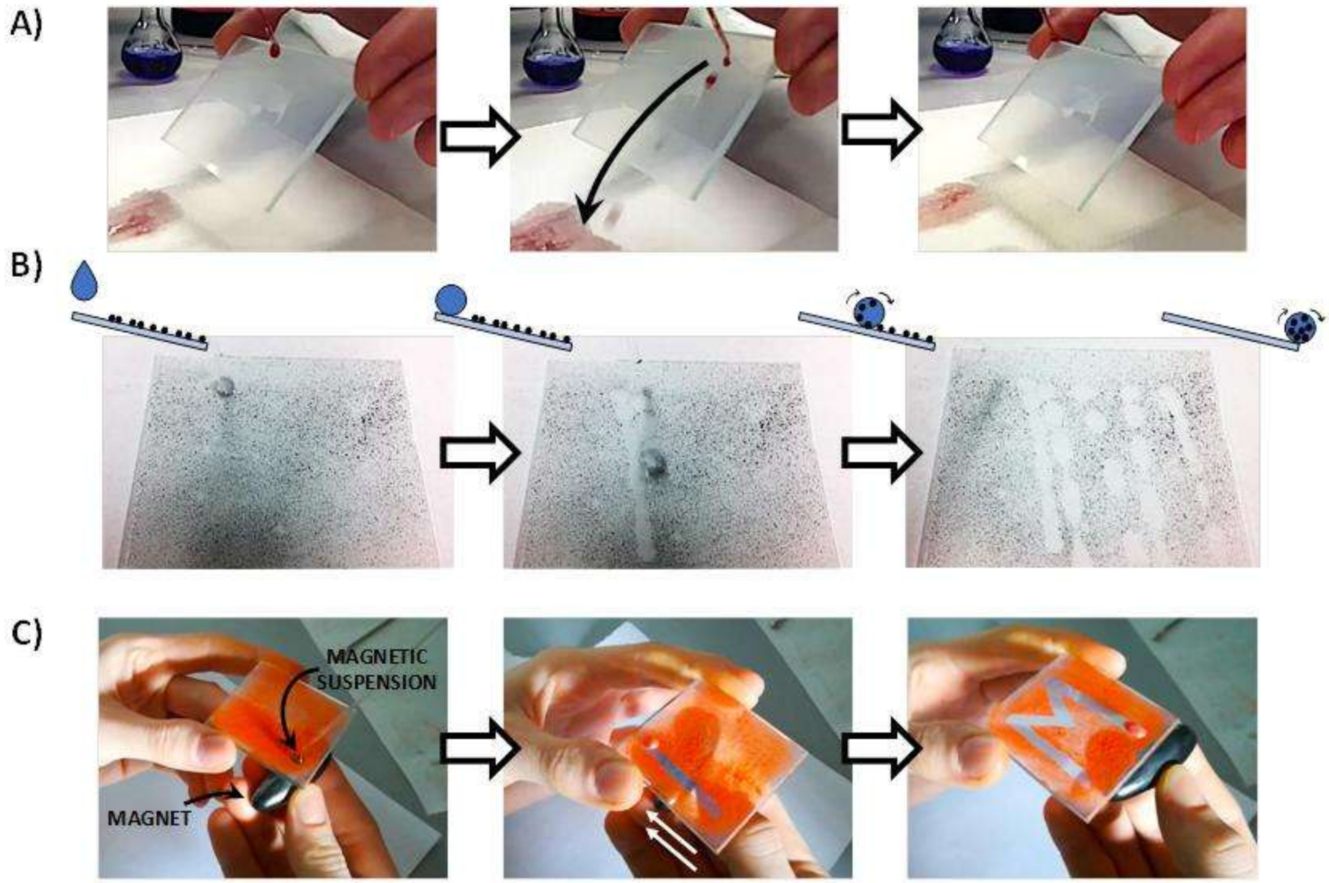

Figure 4. (A) Anti-stain properties: wine is poured on the superhydrophobic coating, which repels it leaving a clean surface. (B) Self-cleaning properties: the hybrid coating covered by graphite powder is easily cleaned by dripping water onto its surface; a schematic depiction of the self-cleaning effect displayed by droplets rolling off the surface, is reported. (C) Liquid transport properties: an aqueous suspension of magnetic particles can be moved at will across the superhydrophobic coating surface using a magnet; the movement is highlighted by covering the surface with methyl orange powder, which is then removed by the moving droplet.

As previously mentioned, the prepared superhydrophobic surfaces can also be adopted to perform photocatalytic lithography according to the procedure reported by Rimoldi *et al.*[25]

The superhydrophobic features can be conveniently displayed also by depositing the hybrid coating on a glass Petri dish: with respect to glass slides, the enclosed walls of the Petri dish make easier to demonstrate the dynamic properties of the non-sticking droplets (rolling-off and bouncing of droplets of water and aqueous solutions), as shown in a video in the Supporting Information. This latter approach is very engaging and it is well suited also for demonstrations at science fairs and other events.

Follow-up assessment

This experimental activity was tested by a class of Master's students in Chemical Sciences and Industrial Chemistry during the course of "Physical Chemistry of Disperse Systems and Interfaces". The hands-on activity is also suitable for students with very limited lab experience, such as high school students. Thanks to its immediate and tangible results and to the limited required equipment, this laboratory experience is well suited for public engagement activities. It was tested by over 40 high school students from different backgrounds during orientation courses and also by 75 high school teachers during refresher training courses. Before the hands-on activity, a one-hour seminar introduced the participants (high school students and teachers) to the basic concepts of surface science and wetting modification. The laboratory experience was successfully performed by all groups (Master's students, high school students and teachers) and it was rated very high in terms of participant appreciation: 35 participants to the wetting seminar and hands-on activity ranked it the most appreciated among the 4-day refresher training course. For its simplicity, commonly available instrumentation, engaging and compelling results, this experience can be easily adapted to a wide range of teaching courses and outreach events, including science festivals.

Participants satisfaction was gauged differently depending on the group. Master's students were required to write a report concerning the laboratory activity in order to evaluate their understanding of its theoretical basis. The final course exam also included a question related to the laboratory experience and the students were later asked to complete a brief multiple-choice test, reported in section S7. The average score was 3.5/5, while the self-evaluation regarding the understanding of theory and applications registered an average score of 4.3 and 4.4 respectively. Overall, students showed a good understanding of wetting phenomena, which profited from directly experiencing the preparation and applications of superhydrophobic surfaces and comparing their properties with conventional hydrophobic and hydrophilic materials.

A survey of the high school teachers' impressions of the refreshing activities showed a high degree of appreciation for the present hands-on activity. In the survey, some of the teachers noted that they lacked rotary evaporators to carry out the activity in their school's laboratories. A few of the high school teachers later requested assistance to repeat the activity to their students and some of them subscribed their classes when the activity was repeated as orientation course for high-school students.

CONCLUSIONS

This hands-on activity serves the purpose of introducing students of various levels and backgrounds to the concept of wetting, the first step towards the study of surface chemistry. This compact and easily reproducible experience shows the properties and potential applications of superhydrophobic materials. The surface functionalization of oxide particles with alkylsilanes was exploited to create hybrid coatings displaying Cassie-Baxter behavior via a simple and quick deposition method. The superhydrophobic coatings, along with reference hydrophobic, hydrophilic and superhydrophilic surfaces, were tested to investigate their anti-stain, self-cleaning and liquid-transport properties. Participants greatly appreciated the engaging and tangible results and the possibility of documenting their experience by taking pictures and videos with their smartphones. The application oriented character of the activity, along with the use of every-day materials, makes it suitable for teaching laboratories as well as public engagement activities.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI:

10.1021/acs.jchemed.XXXXXXX. [ACS will fill this in.]

List of reagents; list of materials and equipment; student handouts; images of application tests on reference surfaces; learning objectives; concepts questions and answers (DOCX)

Video displaying the anti-stain and self-cleaning properties of the superhydrophobic coating on a Petri dish; video showing the liquid transport application (MP4)

AUTHOR INFORMATION

Corresponding Author

*E-mail: daniela.meroni@unimi.it

ORCID

Daniela Meroni: 0000-0002-3386-9293

Notes

The authors declare no competing financial interest.

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