Wetting modification by photocatalysis:

A hands-on activity to demonstrate photoactivated reactions at semiconductor surfaces

Luca Rimoldi[a,b,*], Tommaso Taroni[a,b], Daniela Meroni[a,b,*]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 21033, Milano, Italy.

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

* Corresponding authors: luca.rimoldi@unimi.it; daniela.meroni@unimi.it

Abstract

We present a hands-on activity designed for advanced Physical Chemistry courses for Master's students, on the application of photocatalysis to the modification of the surface properties of a semiconductor (titanium dioxide). The wetting properties of TiO_2 films, deposited from commercial powders, are studied before and after UV irradiation. Irradiation-induced superhydrophilicity is exploited to provide antifogging properties. The TiO_2 films are then functionalized with a perfluorinated alkylsilane to impart superhydrophobicity and subsequently lithographed by irradiation through a photomask: the photocatalytic degradation of the organic chains in the irradiated areas leads to a wetting contrast that can be revealed using dye solutions. This experience can be easily adapted to be suited for undergraduates or high-school students, as well as to demonstrations for science festivals.

Keywords

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

Introduction

Since the discovery of the photoactivity of titanium dioxide (TiO_2) by Fujishima and Honda in 1972[1], photocatalysis has gained ever growing attention for applications in fuel production, pollutant remediation and energy conversion[2,3]. More recently, researchers have started to explore the photocatalysis application to the modification of surface properties, such as wetting phenomena[4]. This exciting research field has led to the development of materials with enticing surface properties, both superhydrophobic and superhydrophilic, which have found widespread application such as antifogging mirrors, self-cleaning ceramics, anti-stain fabrics, anti-corrosion coatings[5], liquid transportation and separation devices[4], but also new lithographic techniques for application in offset printing[6]. These materials have widespread potential application in everyday life and are based on clearly appreciable and immediate phenomena.

The application of photocatalysis to the tailoring of wetting phenomena is well suited to provide engaging activities for students of all levels, which can introduce the general concepts of photocatalysis in a more tangible and immediate/compelling way than conventional experiments such as pollutant degradation[7–10]. Moreover, very few works have proposed teaching laboratory activities on the modification of wetting properties of oxide materials by chemical[11–13] or physical[14] means. Physical chemistry courses for both Bachelor's and Master's students rarely deal with these concepts and few practical experiences that can provide basic knowledge by adopting easy experimental procedures are reported.

Here, we report a hands-on activity focusing on the modification of the TiO_2 surface properties by photocatalysis. On one hand, the effect of light irradiation on the wetting properties of pristine TiO_2 surfaces is investigated for antifogging applications. On the other hand, the photocatalyst surface properties are modified by grafting with alkylsilanes and then patterned films with wetting contrast are prepared by photocatalytic lithography to obtain the site-selective adsorption of dye molecules.

This can be adopted as a laboratory activity for both Master's courses in photochemistry and physical chemistry of colloids and interfaces. This activity was tested by 33 students of the first year of the Master's degrees in Chemical Sciences and Industrial Chemistry during a teaching laboratory of the course 'Physical Chemistry of Disperse Systems and Interfaces'. The activity was performed at mid-semester after an introductory lecture. Thanks to the procedure simplicity, inexpensive instrumentation and tangible results, this experience could be easily adapted to be suited for undergraduates or high-school students, as well as to demonstrations for science festivals.

Experimental overview

Photocatalysis is a physicochemical process in which a semiconductor (photocatalyst) promotes oxidation and reduction reactions upon activation by light of suitable wavelength. The electronic structure of a semiconductor presents a low-energy valence band, where the vast majority of the electrons generally stay, and a high-energy conduction band, to which electrons can be promoted upon light absorption. The most commonly employed photocatalyst, TiO_2, has a band gap ≥3.0 eV, thus UV light is needed to elicit the electron promotion and activate the semiconductor. The electrons excited in the conduction band and the electron vacancies left in the valence band (usually referred as holes) can migrate and reach the surface, where they can promote reduction and oxidation reactions, respectively. Highly reactive species and radicals (mainly hydroxyl and superoxide anion radicals, but also small amount of H_2O_2) are produced by reaction of the photogenerated charge carriers with O_2 and H_2O (Figure 1).

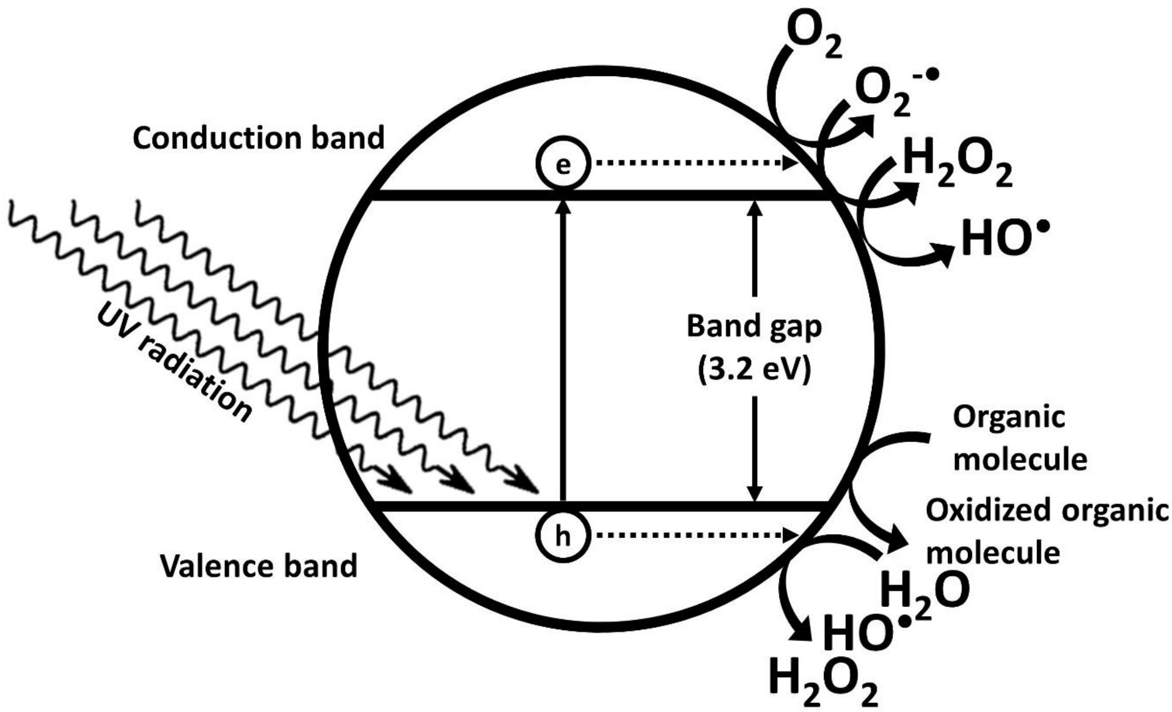

Figure 1 – Schematic representation of the photocatalytic process.

The TiO_2 surface is hydrophilic since it exposes polar moieties such as hydroxyl groups, which can form strong interactions with water. By UV irradiation, the hydrophilicity of TiO_2 surfaces can be enhanced, leading to complete water spreading (*superhydrophilicity*). The origin of this phenomenon has been highly debated in the literature: among the possible explanations that have been proposed there are the photo-activated degradation of adsorbed contaminants, the light activated promotion of surface hydroxylation driven by the formation of surface Ti^{3+} centers[4] and the decrease of the surface tension of H_2O clusters followed by H_2O desorption from TiO_2 surfaces during UV irradiation; the latter was found to play a major role as the driving force behind the photo-driven phenomenon[15].

The surface hydroxylation of TiO_2 can be exploited to graft alkylsilane derivatives via the formation of Si–O–Ti bonds (Figure 2), conferring hydrophobicity to the oxide surface[16]. By this approach, water contact angles higher than 150° (*superhydrophobicity*) can be achieved when films made of TiO_2 micro/nanoparticles are functionalized with long-chain or perfluorinated alkylsilanes. The resulting superhydrophobic behavior is due to the combination of inherently hydrophobic alkyl/perfluorinated chains and of the surface roughness imparted by the TiO_2 micro/nanoparticles, according to the Cassie-Baxter model[17].

Photocatalysis offers a tool to prepare patterned surfaces with superhydrophobic/superhydrophilic contrast[18–20]. By irradiating through a photomask a TiO_2 film functionalized with alkylsilanes (Figure 2), the alkyl chains can be degraded in the light-exposed areas, leading to superhydrophilic patches[21]. The film parts covered by the photomask are instead unaffected, retaining the superhydrophobic behavior. The resulting wetting contrast can then be revealed by pouring an aqueous solution onto the patterned surface.

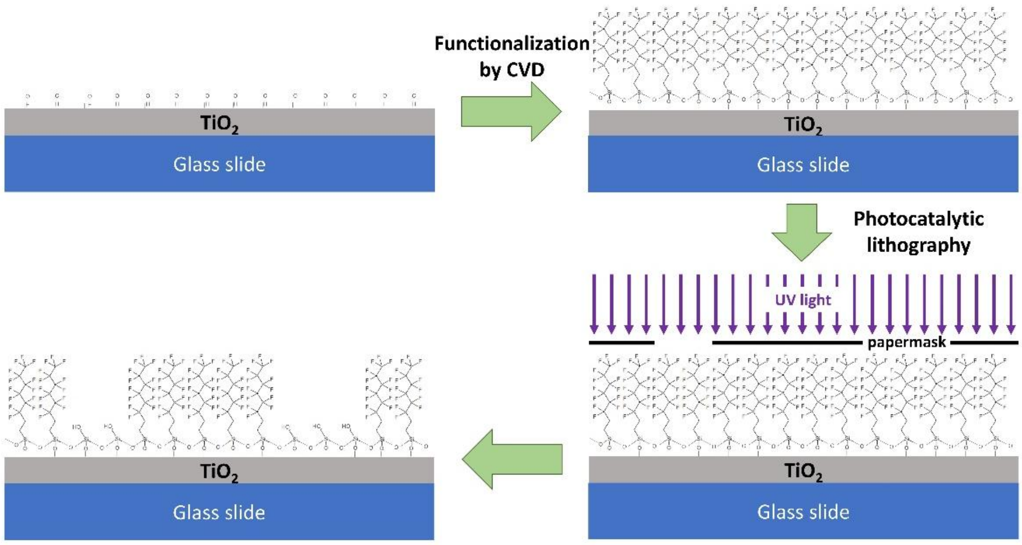

Figure 2 – Schematic of the TiO_2 film functionalization and photocatalytic lithography.

Materials and Instrumentation

Commercial titanium dioxide (Aeroxide® TiO_2 P25) was purchased from Evonik. Acetone, 2-propanol, *1H,1H,2H,2H*-perfluorooctyl-triethoxysilane (PFOS) and bromophenol blue were acquired from Sigma-Aldrich. Doubly distilled MilliQ water was used to prepare the dye solutions.

The chemical vapor deposition (CVD) requires a 20 cm Pyrex glass Petri dish and an oven. Lithographic experiments were optimized using a 500 W iron halogenide lamp (Jelosil HG500); although they were not tested in this instance, less powerful UV lamps (*e.g.*, UV torches or TLC lamps)[22] might be employed by increasing the irradiation time. Film deposition was carried out on soda lime glass slides, using a spin coater (SPS-Europe). Cleaning of the supports and suspension preparation were carried out using an ultrasonic bath. Contact angle measurements were performed on a Krüss EasyDrop instrument.

Hazards

PFOS is irritant for eyes and skin. Safety gloves and lab coats should be worn during the sample preparation. Due to the use of volatile solvents (2-propanol, acetone), the film deposition procedure should be conducted under a fume hood. Safety goggles and gloves must be worn while using the UV lamp, since UV light is dangerous for eyes and skin.

Experimental procedure

Preparation of the TiO_2 films

Five glass slides (5 x 5 cm^2) are cleaned by sequentially sonicating in acetone, 2-propanol and water, then dried on a hot plate. A TiO_2 suspension in 2-propanol (0.5 g in 10 mL) is prepared by sonication. TiO_2 films are deposited by dispensing 2 mL of the TiO_2 suspension drop-wise on the glass slides, then spin coating adopting the following parameters: rotation time 20 s, rotation rate 3000 rpm and rotation acceleration/deceleration 500 rpm/s. After the deposition, the films are dried in an oven at 80°C for 5 min to remove any solvent residual. Alternatively, the TiO_2 films can be deposited by drop casting using a less concentrated TiO_2 slurry, although in that case a higher PFOS amount might be necessary for the functionalization.

Functionalization of the TiO_2 films with perfluoroalkylsilane

The functionalization of TiO_2 films is carried out by CVD (Figure 3a), according to a previously reported procedure[23]. Two of the TiO_2 films are placed on a Petri dish base together with a Teflon cup containing 250 μL of pure PFOS (Figure S1). The Petri dish is then covered with its lid to create a closed chamber (Figure 3b), which is placed in an oven at 100°C for 2 h. The films are then removed from the oven and allowed to cool at room temperature before measuring their water contact angle.

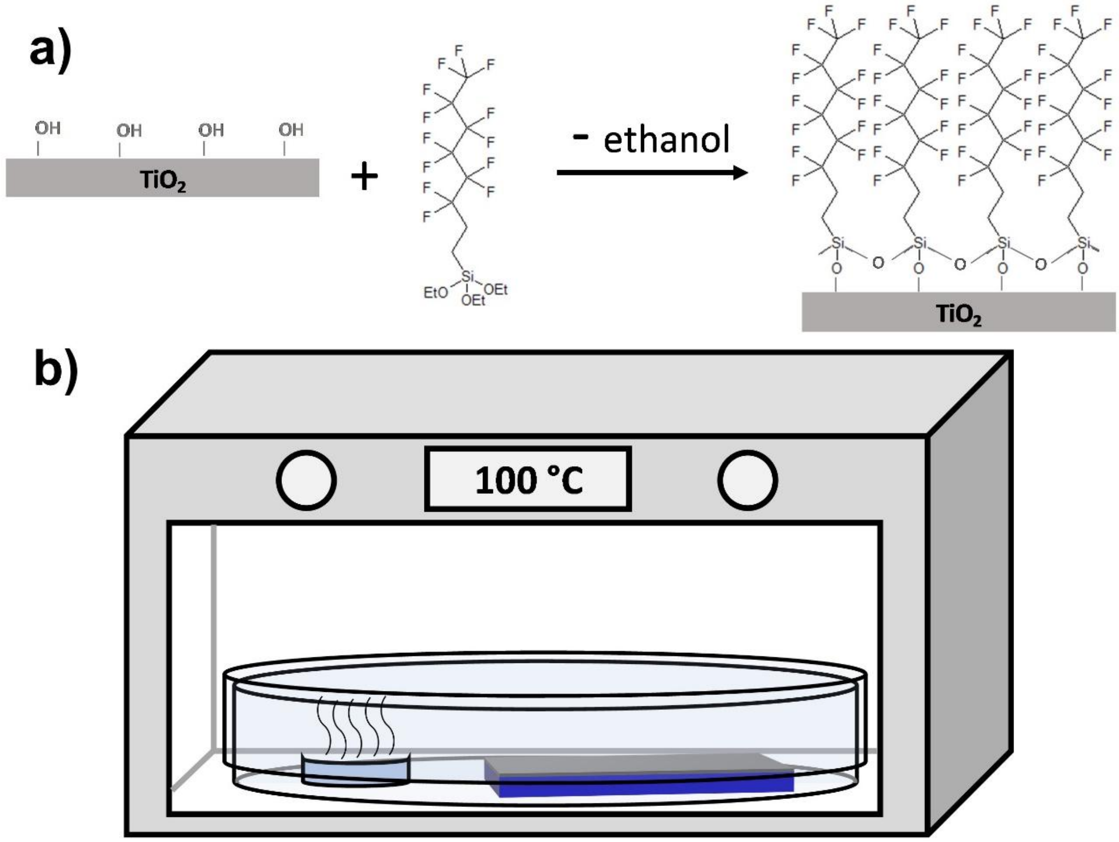

Figure 3 – Reaction of TiO_2 films with PFOS (a); CVD experimental set up (b).

Antifogging properties

One of the bare TiO_2 films is irradiated for 30 min under UV light, while the other is kept in the dark. The water contact angle of the two films is measured (using 5–10 μL droplets) and compared with that of the glass slides. Then, the antifogging properties of the irradiated and non-irradiated films are tested. The film fogging is promoted by placing the TiO_2 layers over a beaker filled with hot water.

Photocatalytic lithography

One of the functionalized TiO_2 films is covered with a photomask, prepared by cutting the desired pattern in a paper sheet. Then, the covered film is irradiated under UV light for 45 min. At the end of the irradiation step, the wetting contrast between the mask-covered areas (remained superhydrophobic) and the exposed regions (become superhydrophilic) is highlighted by depositing a dye aqueous solution (10 mg in 100 mL).

Results and discussion

Student experience

The activity was performed in small groups and required 4 hours. The participants first deposited the TiO_2 films and functionalized two of them via CVD. During the time required by the CVD, students became familiar with contact angle measurements, performed antifogging tests on the pristine TiO_2 films, prepared the dye solution and designed their own photomasks. The activity showed excellent reproducibility among all the students' groups, who documented their results using photos and videos later implemented in a laboratory report.

Antifogging properties

Water contact angles were measured using a digital contact angle goniometer equipped with a software-controlled microsyringe. In case an instrument for contact angle measurements is not available, students can dispense the water droplets using micropipettes, then they can acquire the droplets images using a smartphone or a camera with a magnifying lens and determine the water contact angle between the surface and the tangent to the droplet profile, using a free goniometer software or app, such as BeforeOffice Snap.

Water contact angles of glass slides were 18°±2°, while those on pristine TiO_2 films before and after irradiation were 12°±2° (Figure S2) and <5° (complete spreading), respectively (Figure 4, insets). Antifogging properties mirrored the observed differences in water contact angle. The bare glass surface got immediately covered in droplets upon steam exposure (Figure 4a), impairing the glass transparency. In the case of non-irradiated TiO_2 films, fogging effects were still appreciable. Care must be taken to avoid accidental exposure of the TiO_2 films to direct sunlight or powerful lamps before the experiment to avoid inducing superhydrophilicity also in the non-UV irradiated film. After irradiation under UV lamp, TiO_2 films showed instead excellent antifogging behavior (Figure 4b): irradiated films retained their visual clarity upon steam exposure, as condensed water droplets immediately spread onto the TiO_2 surface creating a continuous water film.

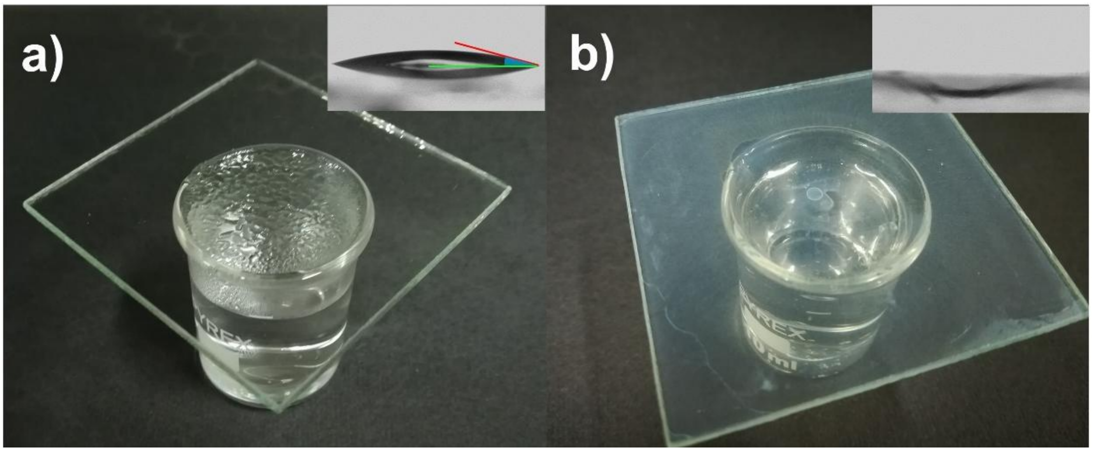

Figure 4 – Fogging of a glass slide placed over a hot water beaker (a). Antifogging properties of a UV irradiated TiO_2 film (b). Insets: corresponding water contact angles; in the case of the irradiated TiO_2 film, no droplet profile can be appreciated due to the complete spreading of

water.

Surface functionalization and photocatalytic lithography

TiO_2 films were functionalized by CVD using a perfluorinated alkylsilane, PFOS. The grafting mechanism involves the formation of silanol moieties from the reaction of PFOS with trace amount of water adsorbed onto the film surface; then silanols undergo condensation reaction with surface hydroxyls and with neighboring silanol molecules, giving rise to a grafted organic layer that imparts hydrophobic properties to the TiO_2 film. The observed contact angles were 160°±2°, characteristic of superhydrophobic materials and indicative of the formation of a Cassie-Baxter state. The measurement of such high contact angles can be complex, as water droplets tend to roll away before any measurements can be performed. In these cases, instead of dispensing a water droplet onto the solid surface using the syringe, the substrate should be lifted till it contacts the water droplet hanging from the syringe tip.

PFOS can be replaced by the less expensive non-fluorinated octyltriethoxysilane, although in this case the resulting contact angles might be lower[23].

The functionalized superhydrophobic films were patterned using the photocatalytic lithography technique. Several materials can be used for the photomask preparation (*e.g.*, paper, metals, …) if they are effective in shielding UV light. Students really enjoyed the creation of photomask from their own design (Figure 5). The wetting contrast can be revealed dripping water or a dye aqueous solution onto the film (see video in the SI).

The lateral resolution of the technique can be investigated by using photomask grids with controlled spacing and revealing the wetting contrast using the steam condensation on the film surface and an optical microscope.

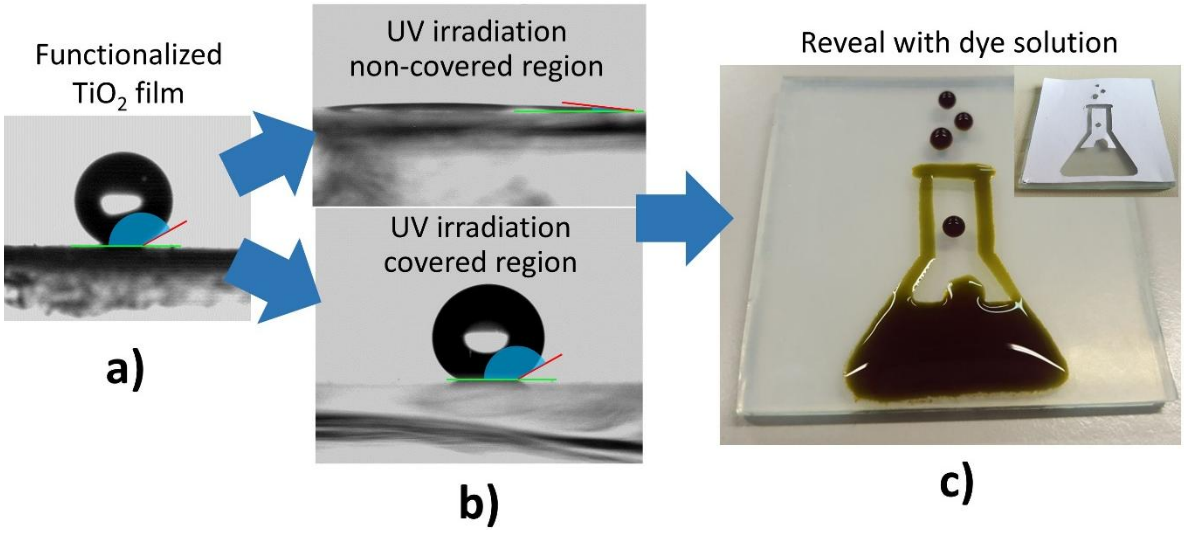

Figure 5 – Water contact angles of the functionalized TiO_2 film before irradiation (a); difference

between covered and non-covered regions of the film after irradiation using a photomask (b); a picture of the resulting patterned surface after revealing with a bromophenol blue solution (c) (inset: photomask design).

Follow up assessment

At the end of the laboratory activity, students were asked to write a report, aimed at evaluating their learning level. Moreover, since the experience was part of a Master's degree course, the final exam included some questions pertaining the laboratory experience. Additionally, a survey was held to gather students' impressions (see Supporting Information): the overall reception was positive, scoring an average of 8.6 /10, and all students were keen on recommending this activity to others. Generally, students were satisfied with the provided theoretical explanations and the overall organization. In particular, some of them underlined that time schedules were respected and no hurdles were encountered; this may suggest the experience can be easily adapted for undergraduates as well. However, few students found the functionalization time too long: the dead times could be put to use by further explaining to the students the theory and applications of photocatalysis and superhydrophilic/superhydrophobic materials.

Conclusions

This hands-on activity displays photocatalysis potential to modify the wetting properties of TiO_2 films. Functionalization with alkylsilanes and UV irradiation were exploited to obtain superhydrophobic and superhydrophilic TiO_2-based films, respectively. The combination of the two treatments was also adopted to create patterned surfaces via photocatalytic lithography. The aim of the experience was to introduce students to photocatalysis basics and give them a grasp on surface science, mainly related to wetting phenomena. An engaging atmosphere was achieved by relating theoretical aspects and experimental work to everyday applications, thus improving the learning process, as demonstrated by the students' positive response.

Associated content

Supporting Information

List of adopted reagents and materials; experimental procedures with theoretical background and notes for students; learning objectives; concepts questions and answers; students' impressions survey; video showing the formation of the image on a lithographed film and its wetting contrast.

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