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Superhydrophobic Polystyrene by Direct Copy of a Lotus Leaf

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Abstract In this paper, we report the realization of an artificial biomimetic superhydrophobic polystyrene (PS) surface by direct copy of a natural lotus leaf, using a simple template method at ambient temperature and atmospheric pressure. We characterized the water sliding behavior by measuring the contact angle (CA), sliding angle, sliding volume, and sliding speed (SS) of the lotus leaf (CA=153.4°, SS=319.4 mm/s), copied lotus leaf, negative silicone template, flat silicone and PS control surfaces, and final PS artificial leaf (CA=149.0°, SS=416.7 mm/s); the last one displays properties comparable with those of lotus. This template method needs neither expensive instruments nor complicated chemical treatments. An adequate optimization of this molding process into automated industrial procedures will lead to a new, innovative, cheap concept for the large-scale industrial development of superhydrophobic surfaces, also starting from their intrinsically hydrophilic counterparts, as here demonstrated for PS.

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1 Introduction

The ability of some natural leaves to stay un-wetted (superhydrophobic) and dirt-free (self-cleaning) came to be evident more than 2,000 years ago; however, only in the twentieth century scientists studied these two correlated phenomena on some natural leaves, focusing on their natural morphologies [1–3] correlated with surface roughness [4–13], surface adhesion [14–16], friction [17], and self-cleaning [18]. The most famous is lotus (*Nelumbo nucifera*), on which "raindrops take a clear, spherical shape without spreading, which probably has to be ascribed to some kind of evaporated essence", as yet Goethe described in 1817 [19]. Superhydrophobicity and self-cleaning are said to be correlated but this correlation do not always appear in nature. For example, the water ferns of *Salvinia* reveal trichomes and waxes, as surface micro- and nano-structures, which lead to a superhydrophobic property of the surface even if the self-cleaning is absent [13].

After a good comprehension of these underlying properties from nature, the next step was to implement them man-made technology: this process is well-known as biomimicry, from the Greek word *biomimesis* which means mimic life. As a matter of fact, micro-, nano-, and micro/nano-patterned superhydrophobic surfaces have become one of the most popular research topics in engineering [20, 21]. Due to the superhydrophobicity and self-cleaning characteristics of its surfaces, the natural lotus leaf has been intensively bio-mimed [20, 22–24] and a number of methods have been applied to fabricate such artificial surfaces mimicking the natural morphology: by the fabri-

cation of nano- (micro-) protrusion by reactive ion etching [20], creating structured coatings similar to the lotus leaves from polyelectrolyte multilayer films [25], making a nickel mold via electroforming and UV-nanoimprint lithography [24, 26, 27]; by adding ethanol to PS solution [28], producing polydimethylsiloxane (PDMS) replica molding with photolithographically manufactured micro-patterned masters [29], nano-casting PDMS [22]; by soft-lithography method of polymethylmetacrylate replica using PDMS molds [30], developing the dental wax cast technique [31] of a replica with polyether (PE) [23], polyvinylsiloxane [32], conventional lacquer [5], epoxy resin [33, 34], the artificial surface patterning [35–45], the chemical surface modification [46–48] or a combination of both morphological and chemical modifications [49–51]. On the contrary, only six patents for invention, with "self cleaning "and" super hydrophobic" as keywords, have been duly deposited during the last 6 years at the European Patent Office, thus with a current rate of one European patent per year.

From the literature, the superhydrophobic and self-cleaning properties have been evaluated only by the measurement of the contact angle (CA) and the contact angle hysteresis (CAH), which can be more easily quantified by the tilting angle (TA) [17, 22, 28, 29]. By definition, a high CA and low CAH (or TA) denote a superhydrophobic and self-cleaning surface [13, 17, 22, 27]. However, it was highlighted that a more, than the maximum CA, important parameter to determine when a surface is superhydrophobic is TA, due to its correlation with the driving force of a liquid drop [9]. In a previous work of our group [52], we introduce other two parameters —the sliding volume (SV) and the sliding speed (SS)—as additional indexes of the superhydrophobicity and self-cleaning property of a surface; this was motivated by the fact that SV and SS are straightforward and direct measurements of the surface water-repellency and self-cleaning ability, in both static and dynamic regimes. Moreover, we have defined the drop minimum volume and the corresponding sliding speed with respect to a vertical surface very close to the real condition of use (i.e., glass windows, external building coverings, internal faces of refrigerators or freezers, surfaces of bathroom fittings or tiles, etc.). A high CA, low CAH (or TA), low SV, and high SS denote a superhydrophobic and self-cleaning surface.

Referring to previous scientific works on lotus leaf, only few papers deal with the replication of its surface structures (convex cell papillae but not 3D wax crystals) by molding [22, 24, 26, 27], such as the present study.

In this study, we readily obtained a biomimetic lotus-leaf-like polystyrene (PS) superhydrophobic surface by replicating the morphological surface pattern of a natural lotus leaf. The molding method used in this study is similar to that reported in previous published works [9, 22] but, to our knowledge, our method is the first capable of creating a superhydrophobic lotus-leaf-like PS surface using a template method at ambient temperature and atmospheric pressure (no controlled temperature/vacuum condition was necessary). We elaborate on the definition of what is a superhydrophobic and self-cleaning surface, taking into account not only the classical parameters (CA and TA), but also the SV and SS parameters of a drop rolling down, for a more complete surface characterization of the lotus leaf, copied lotus leaf, negative silicone template, flat silicone and PS control surfaces, as well as positive PS template. Compared with the other above-mentioned methods, our molding technique needs neither expensive instruments nor complicated chemical treatments and is thus a good candidate for industrial applications.

2 Materials and Methods

2.1 Molding Method

Upper leaf sides (adaxial) of freshly lotus plant, cultivated in the "Giardino Botanico Rea" (Turin) associated with the Natural Science Museum of Turin, were used. These leaves (diameter of ~25 cm) are cut and the first copy (C1) deposition was made within 24 h. Figure 1 reported the simple flowchart of the lotus leaf replication process composed by two steps at room temperature and atmospheric pressure.

The molding method uses a silicone elastomer (R39-2186-2, Nusil Technology), a low viscosity hydrophobic silicone, to obtain the first copy C1 (diameter of ~25 cm) of a natural lotus leaf used as the natural template (LL). The lotus leaf resulted after the copying process is named copied lotus leaf (CLL). R39-2186-2 is a two-phase silicone, mixed in the mass proportion of 1:1, when extracted from side-by-side kits through a disposable static mix tip. Both components are extruded directly onto the lotus leaf and immediately spread with a stick to form a few millimeters high silicone layer on the substratum. After polymerization, the negative mold can be easily peeled off from the surface, giving rise to C1. Without any other intermediate treatment, C1 was directly used for preparation of the positive mold, called C2. Need to say, the low viscosity of the silicone R39-2186-2 does not require any pressure to replicate the smaller structures on the leaves, contrary to the molding methods already described in the literature [24, 26, 27, 53].

A commercial hydrophilic PS sheet was reduced into small particles without any further treatment. A volume of 20 ml tetrahydrofuran solvent was added to 1 g of PS and then the solution was stirred with a heating magnetic stirrer

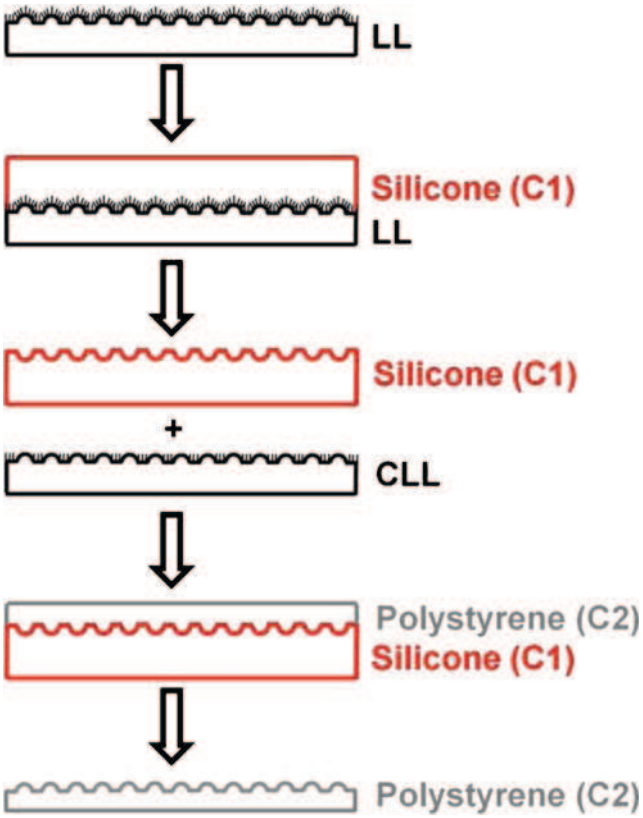

Fig. 1 Schematic illustration of our lotus leaf replication process, composed of two steps at room temperature and atmospheric pressure

(Are—Velp) for 20 min with an increasing speed (5 min at 600 rpm, 5 min at 720 rpm, and 10 min at 840 rpm) to form a uniform solution at ambient temperature and pressure. The solution was directly cast on a 9-cm diameter subarea of the negative silicone template (C1). After solvent volatilization for 24 h in the atmosphere at room temperature, a double adhesive was applied on a rigid substratum, the PS positive template (C2) was attached on the double adhesive and then the silicone negative template was peeled off from the C2 positive one (diameter of ~9 cm). As a result, the surface micro-structure of the lotus leaf was transferred to the PS surface on the side contacting with the silicone.

Two control surfaces have been necessarily characterized to establish the reference intrinsic parameters for comparing between C1 and C2: R39-2186-2 silicone or the PS/20 ml-tetrahydrofuran solution was cast on a cleaned silicon wafer in 100% ethanol and sonicated and, after 24 h polimerization (volatilization), we obtained flat silicone or PS surfaces, called C1_control or C2_control.

2.2 Surface Characterization

We observed the surfaces of LL, CLL, C1, and C2 by means of a field emission scanning electron microscope (FESEM, Zeiss SUPRA 40 for LL and CLL or FEI-Inspect^{TM} F50 for C1 and C2) equipped with a field emission tungsten cathode. Samples of ~0.5 cm^2 were obtained, fixed to aluminum stubs by double-sided adhesive carbon conductive tape (Nisshin EM Co. Ltd.), used as these were (except for C1, cleaned with ethanol) and air-dried. Samples LL and CLL (C1 and C2) were Cr(Au-Pd) coated, approximately 10 nm in thickness. Referring to LL and CLL, no fixation processes were made to avoid alteration of the wax crystals [2].

2.3 Wettability Measurement

The wettability of LL, CLL, C1, C1_control, C2, C2_control surfaces was determined by measuring the static CA of distilled water droplets over the samples, fixed to a horizontal plane by a soft adhesive to keep the samples flat. We consider a series of 20 (five of them were considered in [20, 29, 52]) random volume drops, gently deposited on the

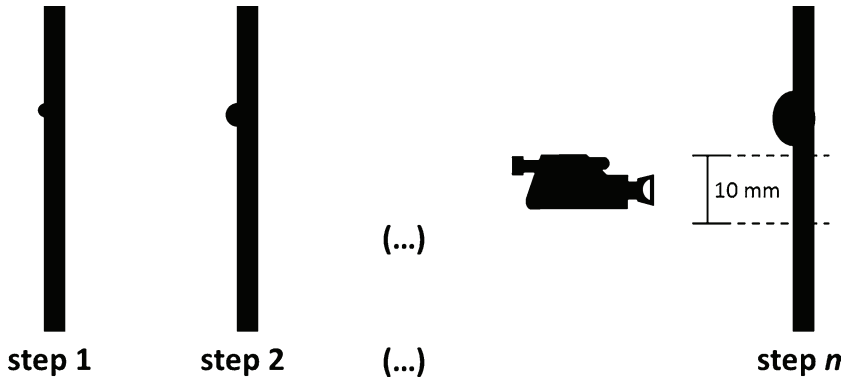

Fig. 2 The step-by-step process to determine the two additional parameters, SV and SS. The specimen stage is fixed vertically (90°) and the drop volume has been increased with 2-μl droplet at each step, from 2 μl up to the minimum sliding volume (SV) of the drop, which is necessary to cause the sliding of the drop (final step, *n*). At this instant, the drop starts to slide and the sliding speed (SS) was determined measuring the time to cover the fixed distance of 10 mm (mean velocity)

LL and CLL (C1, C1_control, C2, C2_control) with a standard single-use syringe. The contact angle was recorded with an OLYMPUS MJU 1010 digital photocamera, measured and statistically analyzed with the software

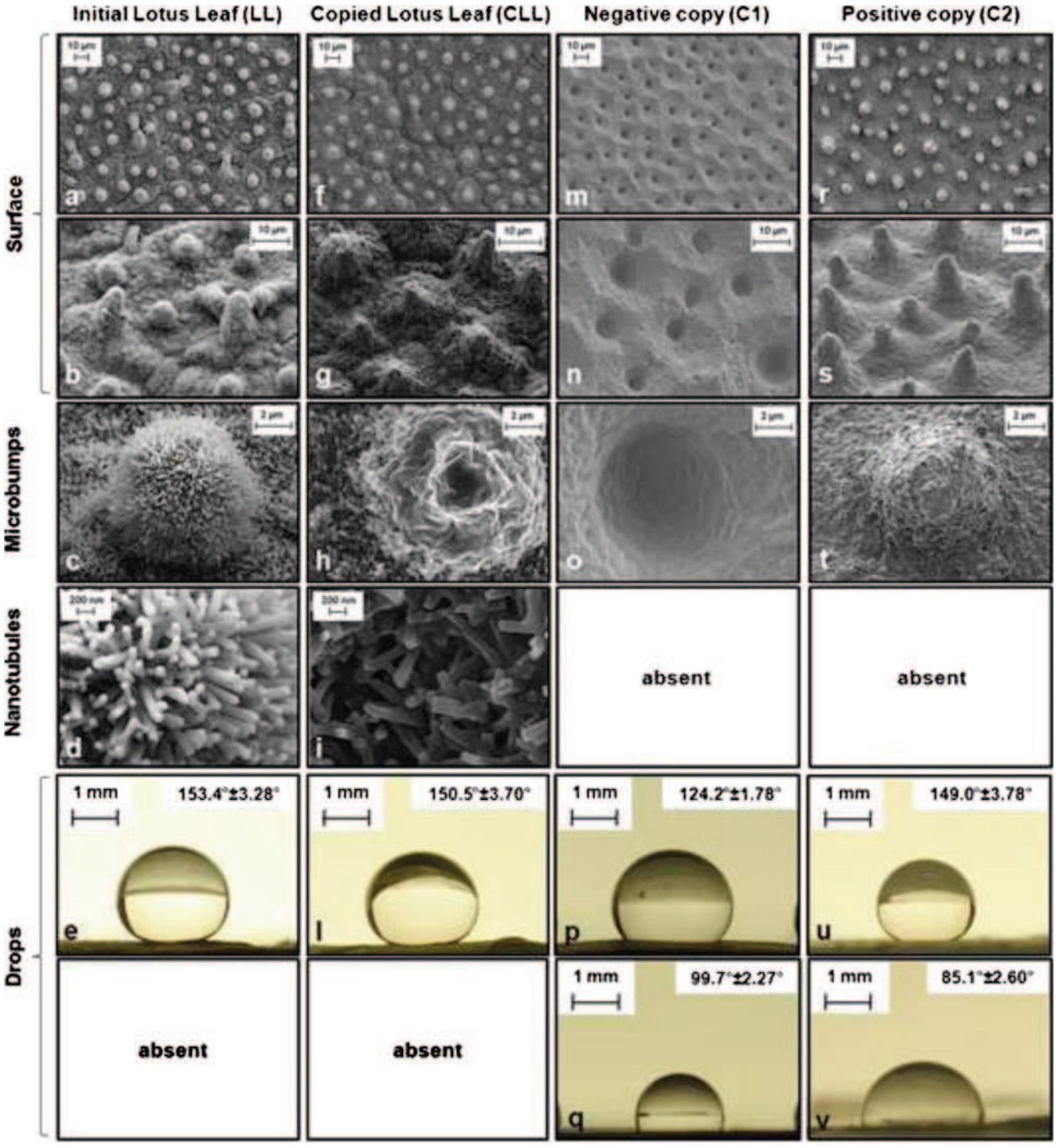

Fig. 3 Details of: **a** the fresh lotus leaf (LL), **f** the lotus leaf resulted after copying process (CLL), **m** the negative copy (C1) and **r** the positive copy (C2). In particular, **b**, **g**, and **s** (**n**) show randomly distributed convex (concave) cell papillae; **c**, **h**, and **t** (**o**) show a detail of the convex (concave) cell papilla and the wax tubules are magnified in **d** (natural wax tubules) and **i** (here the wax tubules are broken due to the C1 deposition and peeling). The nano-tubules are absent on C1 and C2. Water drop on the surface of: **e** the fresh lotus leaf (LL), **l** the lotus leaf resulted after copying process (CLL), **p** the negative copy (C1) and **u** the positive copy (C2). **q** and **v** show the shape of a water drop on C1_control and C2_control surfaces, respectively. For LL and CLL, no control surface can be defined. The measurements reported in **e**, **l**, **p**, **u**, **q**, **v** are the average CA±standard deviation

ImageJ 1.41o. The average CA of the control surfaces was used as the intrinsic CAs of the R39-2186-2 and PS flat surfaces.

Two conceptually distinct procedures were used to evaluate the drop sliding characteristics: (1) fixing the volume of the drop (~18 μl, the diameter of the spherical droplet was ~2.2 mm) and measuring the tilted angle of the sample stage at drop sliding (TA) or (2) fixing the angle of the specimen stage vertically (90°) and measuring the minimum SV of the drop, increasing it step-by-step with 2 μl volume increment. Referring to the second procedure, the sliding speed (SS) of the drop was also determined, measuring the time of the minimum SV drop to cover the fixed distance of 10 mm. Figure 2 schematically shows the step-by-step process to determine the two additional parameters, SV and SS.

3 Results

3.1 Surface Characterization

This technique demonstrates excellent replication ability for convex micro-structures (cell papillae) of the lotus leaf and the replication quality of these micro-structures from LL to C1 and in turn to C2 appears to be high. As shown in Fig. 3 (with the lack of 200-nm-scale bar micrographies for C1 and C2), the nano-tubules (superimposed layer of hydrophobic 3D wax tubules) of the lotus leaf have not been transferred, owing to their permanent removal during the C1 deposition which rules out the possibility of the nano-tubules replication, as reported in other previous studies [5, 23, 24, 26, 27, 30, 53].

3.2 Wettability Measurement

In Table 1, the mean values and standard deviation of wettability measurements are reported; correspondingly, Fig. 3 shows a representative water drop on each surface. The first remarkable result concerns the same CA (~150°) for LL and CLL in spite of the absence of wax nano-tubules over the cell papillae of CLL. When compared to the flat C1_control surface (~100°, intrinsically hydrophobic) and C2_control surface (~85°, intrinsically hydrophilic), the water CAs of corresponding replicas are increased by about 24° (C1 ~ 124°) and 64° (C2 ~ 149°). This finding indicates that the CA of C2 is absolutely comparable with LL, suggesting an excellent CA replication. The C2_control surface of PS has an intrinsic CA closed to the values found in literature (~92° [17], ~98° [28]), while C2 has a CA significantly higher of 45° than that (~105°) reported in [17]. Meanwhile, referring to a PE based (intrinsic CA=102.9°± 4.5) molding method, the CA for C2 could be comparable with those of the PE lotus replica (CA=157.8°±4.2) [23].

The best (so lowest) TA belongs to CLL, 10° lower than the value recorded for LL. The silicone samples, both flat and micro-structured, display a high TA (~74° and ~81°, respectively) and an intermediate value of ~50° was measured by C2_control.

The SV is similar among LL (~5 μl) and CLL (~6 μl) surfaces while increases to ~20 μl for the others. The worst result belongs to C2 (TA not observed, thus >90°).

In spite of this, the SS highlights the goodness of the result obtained for C2, comparable with those of the surfaces LL and CLL. The SS values of C2_control, C1 and C1_control are three, two, and one order of magnitude lower than those of C2, LL, and CLL.

4 Discussion

The described molding technique requires a silicone polymerization time one order of magnitude longer than the fast and similar molding process presented in [53]. Considering live and dried lotus leaves, showing only a little discernible difference (cell papillae are taller on the fresh lotus leaf) in the wettability response [17, 30, 34], a longer time of polymerization is needed for an excellent morphological replication. Its resolution could be quantified into ~1 μm; thus, through this method, nano-structures could not be copied with our considered materials (silicone and PS).

The material of the positive (negative) template is here intrinsically hydrophilic (hydrophobic), while according to the experimental increment of CA, the C2 (C1) replica

Table 1 Contact angle (CA), tilting angle (TA), sliding volume (SV), and sliding speed (SS) of lotus leaf (LL), copied lotus leaf (CLL), first silicone copy (C1), flat silicone control surface (C1_control), second PS copy (C2), and flat PS control surface (C2_control)

	CA (°)	TA (°)	SV (μl)	SS (mm/s)
LL	153.4±3.3	26.2±3.6	4.7±1.1	319.4±97.4
CLL	150.5±3.7	18.0±1.5	6.3±0.8	319.4±97.4
C1	124.2±1.8	80.7±1.3	19.3±0.8	9.7±2.9
C1_control	99.7±2.3	73.9±4.2	21.7±3.4	15.7±12.3
C2	149.0±3.8	>90°	23.0±1.1	416.7±91.3
C2_control	85.1±2.6	48.6±3.3	20.0±0.0	0.1±0.1

becomes hydrophobic (more hydrophobic). Some previous papers reported that the hydrophobic behavior could be achieved from hydrophilic material by increasing the surface roughness [24, 27]. A possible explanation is related to the molding process inducing modification of the topological characteristics, namely the cell papillae of PS replicas: several studies [6, 13] gave evidence that a surface with hemispherical topped asperities, like lotus convex cell papillae, should be the most appropriate to obtain an increment of the CA. On the contrary, if the classical Wenzel model [54] is taken into account, surface roughness increases the hydrophilicity (hydrophobicity) of an intrinsically hydrophilic (hydrophobic) material. As a consequence, Wenzel model could not be correctly applicable to the PS surface while agrees with the observations on C1 surfaces.

According to [26], a surface is self-cleaning if having very high CA and very low CAH, which is usually associated to the Cassie-Baxter [55] regime. We observed on C2 samples that the just-deposited drop stays in a state not conformal to the topology of substratum, in accordance with the Cassie-Baxter hypothesis: however, after only few seconds, the drop becomes conformal with surface topology and thus falls into the Wenzel state, displaying a high CAH/TA. Experimentally, we clearly observed the transition from the Cassie-Baxter to the Wenzel state for the C2 surface (intrinsically hydrophilic, high CA, high TA) as time goes by or due to any external disturbance the specimen stage is subjected to [26] (inducing evaporation and thus pressure increment) or when depositing the droplet from some height [56]. Thus, it seems that in some cases [24, 26, 27, 57–59], including the surfaces presented in this work, the water drops seem to be sticky at high CA (Wenzel state).

Probably superficial irregularities of micro-structures are present on the C2 surface leading to unstable air pockets under the drop which are substituted by water in few seconds. These superficial imperfections, rather than the absence of wax crystal tubules over C2, have probably determined this significant difference between C2 and LL. We suggest such interpretation because in this case, the superimposition of the nano-scale wax tubules to the micro-scale cell papillae on the LL is not expected to supply any significant contribute: as we have verified, CLL shows the absence of wax tubules on the cell papillae and a presence of broken and numerous wax tubules in the areas between cell papillae but still shows the same results of LL in terms of CA, TA, SV, and SS. This finding adds an information to previous works, which highlighted that the complete removal of the wax tubules from the surface halved the CA value [17] while the annealing of wax tubules, keeping the wax composition and quantity nearly unchanged on the micro-patterned surface (this morphology is really close to our C2), determines a 11% diminution of the initial CA of the lotus leaf [34] and a sticky behavior of drops (TA>90°, as here for C2). However, in our case, we have reached a high CA of C2 copy, even if the hierarchical nano-tubules are absent.

According to previous papers [6, 13], we conclude that the presence of hemispherical micro-bumps (first hierarchical level) induces an increment of CA (for C2) and the presence of additional nano-tubules (second hierarchical level) on micro-bumps decreases the CAH so the TA (for CLL). Therefore, such absence of nano-tubules on C2, differently from a lotus leaf, can be supposed to be the reason of the observed high TA and SV with respect to those describing the performance of a natural leaf.

5 Conclusions

We have successfully fabricated a stable biomimetic lotus-leaf-like PS superhydrophobic surface. The CA and the SS of the positive PS copy of lotus leaf are 149.0° and 416.7 mm/s respectively, comparable to those of a lotus leaf (CA=153.4° and SS=319.4 mm/s). As shown by the existing TA and SV limitations (relate to CAH), our method necessitates to be further improved in order to enhance also these last parameters. The replication of the nano-tubules, and thus the improvement of the molding method here presented, appears to be necessary to obtain an even more efficient superhydrophobic and simultaneously self-cleaning surface.

In spite of this, our approach remains very promising for realizing with different materials superhydrophobic synthetic lotus leaves working in static regime (contact angle). Compared to other methods of morphological replication of natural superhydrophobic leaves, this procedure involves ambient pressure and temperature and is much easier, requiring neither expensive instruments nor complicated chemical treatments.

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