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Replication of butterfly wing and natural lotus leaf nanostructures by nanoimprint on Silica Sol-gel films.

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1. Introduction

Nature offers a variety of surfaces with functional properties and is an inspiration source for numerous applications and technologies. Recently, it has demonstrated some biological surfaces are structured at the scale of micro and nanometric for involving different properties as superhydrophobicity or superhydrophilicity [1],[2]. More broadly, researchers are turned around biological systems to create a surface with new functionalities, this field is popularly known as “Biomimetics” [3]. One of these well known applications are the lotus leaves and butterfly wings with their specific structure given a superhydrophobicity or self-cleaning properties [4],[5],[6]. Several studies report both the understanding of these micro and nanostructures and the fabrication of biomimetic structures. One of challenges is to replicate these biomimetics structures over large scales and at affordable price for industrial applications as for example the next generation of windows or windshields, Nano Imprint Lithography is potentially the most promising technique due to its low cost, its less time-consuming and its ability to imprint easily large areas. In this way, Chen and al. has shown in Ref 7 the ability to fabricate a mold from a lotus leaf [7]. The nanoimprint from Lotus leaf mold has been also done on elastomer materials as Polydimethylsiloxane [7] and polymers [8]. Here, we propose one next step with the replication of biomimetic surfaces on highly interesting sol-gel materials by nanoimprint. The structuring sol-gel materials are stable thermally and mechanically and are used in many applications such as coating of glazing, optic materials, biomaterials[9]. We have chosen to imprint the lotus leaf and butterfly wings in order to obtain superhydrophobic surfaces. In this paper, we describe a simple method to fabricate biomimetic and superhydrophobic surfaces which are thermally and mechanically stable. The paper describes first our fabrication method and then discusses the thermal properties of our biomimetic surfaces and the challenges for this technology.

2. Experimental

The replication of the surface of lotus leaf and butterfly wing (Papilionae Ulysse) was carried out from a flexible Polydimethylsiloxane (PDMS) mold into a liquid sol-gel. In the first step, the PDMS molds were prepared by casting a liquid PDMS solution against the surface of lotus leaf and butterfly wing. After solidification at 80 °C for several hours, the PDMS layer was peeled off, resulting in a negative structure of the original templates. In the case of lotus leaf, the release from the

mold was done easily, whereas the scales of the butterfly stay stucked to the PDMS. The butterfly wings being symmetrical, the PDMS mold can be used for the nanoimprint. Methyltriethoxysilane (MTEOS) sol-gel films are deposited by spin coating on glass or silicon substrates. The MTEOS film thickness was approximately 900 nm as measured with a profilometer. More details for preparation of MTEOS sol-gel resist has been described in previous work [11]. Imprint pressure was kept lower than 2 bars and imprint temperature is included between 80 °C and 150 °C for about 20 minutes. All samples of each series have been done with the same mold on a surface of few squared centimetres with a good reliability and reproducibility for imprint. As last step, biomimetic structures, replication of lotus leaf and butterfly wing, were annealed at a temperature between 200 °C and 500°C in steps of 50 °C during 2 hours. For samples with the highest thermal treatment (500 °C), a surface grafting of fluoroalkylsilane was performed by evaporation during 12 hours at 80 °C. All hydrophobic surfaces were characterized by their water contact angle with a droplet of 1 µL on tensiometer.

3. Results and Discussion

The lotus leaf is well known for its superhydrophobic and self-cleaning properties related to a combination of double scale geometries [1],[2]. Our investigation by Scanning Electron Microscopy (SEM) shows the inner structures for lotus leaf with micrometer-scale pillars of 3 to 11 µm diameter and 7 to 13 µm height randomly covered by branch-like nanostructures of about 100 nm diameters (see Figure. 1a and 1b). We measured a density for these nanopillars around $3 \cdot 10^{11}$ pillars per squared meters from SEM images. As expected, angle contact for these structures is measured around 160° confirming a superhydrophobic behavior and a low surface energy. Only waxes have been casted in PDMS mold due to variable directions of nanobranches which can not to be turned it out (Figures 1b and 1d). As an other interest, The cover scales of most of the butterfly *Papilio* species (figure 2a) present a common bulk and surface structure. The upper membrane is constituted by a multilayered air/chitin film of about 5 to 10 periods (Figure 3) and the surface between two ridges is periodically undulated, forming a regular set of concave cavities (figure 2b). According to the species, these cavities are roughly spherical (*Papilio blumei* Boisduval, 1836) or slightly elongated (*Papilio peranthus* Fabricius, 1787). In our case, we investigate Papilionae Ulysse specie for which convex scales, each approximately 100 µm long (Fig 2a). One scale is composed of longitudinal ridges spaced by 5 µm and cross ribs each of 3 to 6

μm (Fig. 2b). The surface of these scales is undulated and forms cisterns between each cross rib [4],[5]. It is also found a superhydrophobic surface for butterfly wings with a contact angle of about 160° close to the value for lotus.

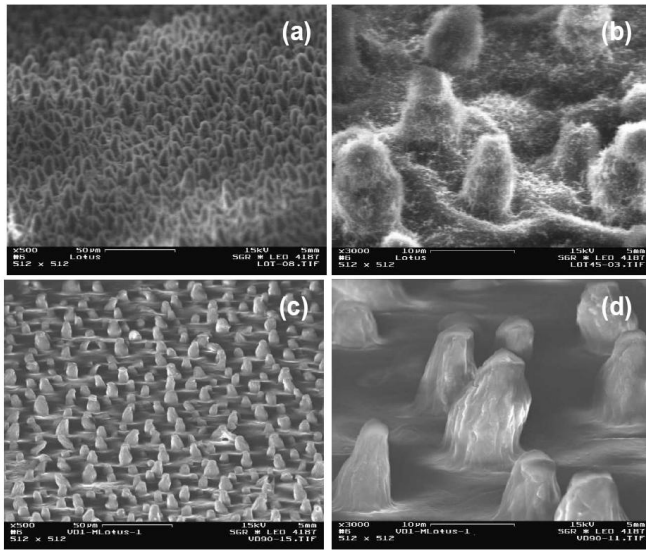


Figure 1: SEM images of the natural Lotus leaf ((a) and (b)) and the replicated surface ((c) and (d)). Angle of view : 75° except for (b) 45° . The scale bar corresponds on (a), (c) to $50 \mu\text{m}$ and to $10 \mu\text{m}$ on (b), (d).

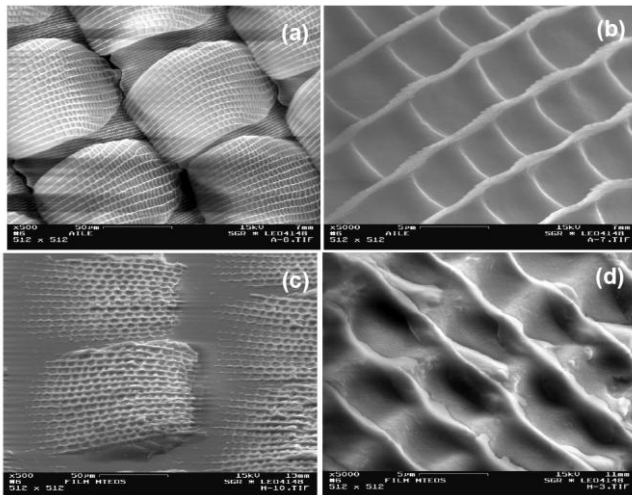


Figure 2: SEM images of the butterfly wing ((a) and (b)) and the replicated surface ((c) and (d)). Angle of view : 45° . The scale bar corresponds on (a), (c) to $50 \mu\text{m}$ and to $5 \mu\text{m}$ on (b), (d).

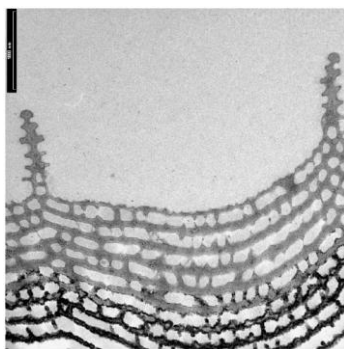


Figure 3: TEM view of a section of the individual cover scale

Replication of surface morphology for both leaf and wings are depicted in SEM pictures 1c, 1d and 2c, 2d respectively. Micropillars of lotus leaf are imprinted with fairly fidelity according to their size and their directions but with lower pillar density than original structures. It is found around 50% of waxes are imprinted due to low thickness of MTEOS films and thus a lack or matter to fill out the PDMS mold. It is expected an initial resist layer around $2 \mu\text{m}$ to fully fill out the imprint stamp.

In the same way, the scales of butterfly wing are successfully imprinted with its ribs and cross ribs on each scale (Fig. 2d). Again, a too low thickness for MTEOS films coupled with the convexity of scales lead to a partial filling of imprint mold and an inhomogeneous imprint along a scale (Fig. 2c). We observed that the filling and imprint of our sol-gel resist is deeper at the centre compared to the extremity of the scale and involve cisterns and hollows with plate bottom at the centre and at the extremity respectively as shown in Figure 4.

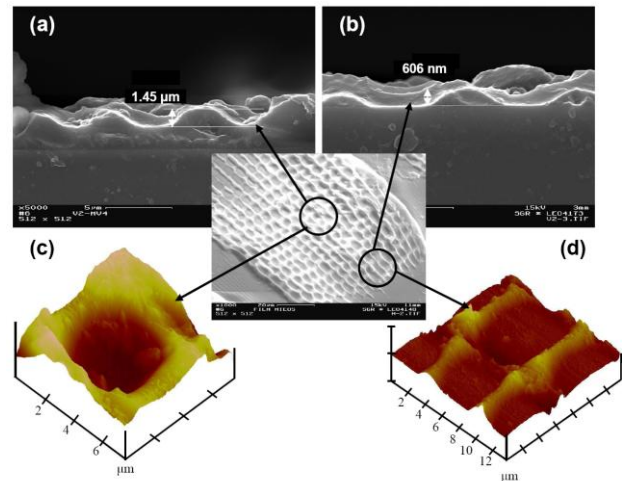


Figure 4: SEM and AFM images of the center ((a) and (c)) and of the extremity ((b) and (d)) of the scale

Hydrophobic behaviour for bioinspired surfaces is characterized by their water static angle contact. When compared to water contact angle on uncoated glass $39 \pm 1^\circ$ and on MTEOS thin film $86 \pm 2^\circ$, it was found that the replicated surfaces showed higher values with same values around $123 \pm 2^\circ$ for lotus and butterfly replications (Fig. 5). That confirms the fabrication at low cost of superhydrophobic surfaces from lotus leaves and butterfly wings. The original low surface energy for unstructured MTEOS films is associated to methyl groups at its surface. These organic groups can be removed by annealing at temperatures higher than 450°C [10]. A transition between hydrophobic and hydrophilic surfaces is thus expected around 400°C where the destruction of methyl groups starts. In the case of imprinted structures, the hydrophobicity is accentuated at low annealing temperatures and as contrary the hydrophilicity increases at higher temperatures. We have observed this transition as shown in Figure 6. We are able to fabricate some patterned surfaces which are tuned from superhydrophobic to superhydrophilic by adequate annealing temperature. In addition, the imprinted surfaces become pure silica structures after total burning of methyl groups around 500°C and bring interesting mechanical and chemical properties [11].

These pure silica imprinted surfaces (annealed at 500°C) are finally grafted with classic fluoroalkylsilane to switch from superhydrophilic to stable superhydrophobic glass surfaces with a contact angle of about 120° for both lotus and butterfly replication. of replicated butterfly surface.

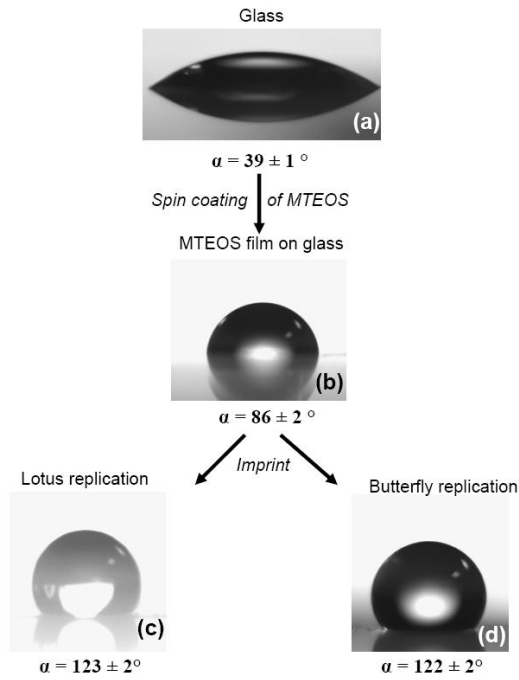


Figure 5: Side profile of a droplet of a water on glass (a), MTEOS film coated on glass (b), replicated surface of lotus (c) and of butterfly (d).

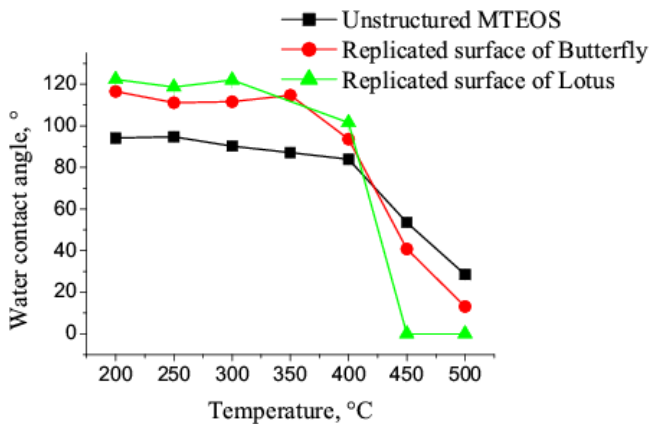


Figure 6: Water contact angle measurements on no structured MTEOS (a), replicated surface of butterfly (b) and replicated surface of lotus (c) as a function of heated temperature.

However, the water contact angle of replicated structures is lower compared to the real natural lotus leaf and butterfly wing. In both cases, the major limitation is the thickness of the MTEOS film. For the lotus leaf replication, the reduced density of pillars allows the water droplet to go between pillars as we observed by environmental SEM microscopy. Nevertheless, we locally observe very high contact angle values ($>160^\circ$) for lotus replication. Indeed, some areas of imprinted lotus samples are so superhydrophobic that it is not possible to deposit a water droplet on it (Fig. 7). The water droplets move to be on other areas where pillars density is weaker. For the butterfly replication, a homogenous imprint along the scale could lead to higher value of contact angle. These results emphasize on the high importance to fabricate thicker and homogeneous sol-gel resist films. Further works are necessary in order to have a higher thickness of sol-gel film, for that a more viscous sol-gel has to be used.

4. Conclusion

An alternative and attractive method for fabrication of superhydrophobic surfaces is reported by biomimeticism of lotus leaves and butterfly wings. The specific behaviour of imprinted silica sol gel materials allow to switch from superhydrophobic to superhydrophilic surfaces only by adequate annealing. These imprinted nano-structured films on silicon or glass substrates are advantageously stable until at high temperature with the formation of pure silica structures. The replicated structures can be covered yet by an adapted interferential multilayer that generates an iridescent color to the glass, without modifying its hydrophobic properties. These works will be presented in a further paper.

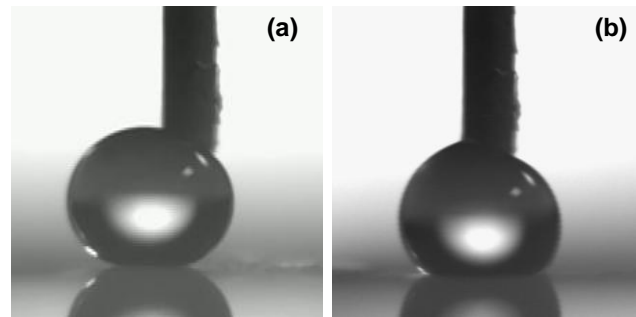


Figure 7: Syringe with water droplet on replicated surface lotus with high pillar density (a) and low pillar density (b).

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