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Replication of butterfly wing and natural lotus leaf structures by nanoimprint on silica sol–gel films

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Abstract
An original and low cost method for the fabrication of patterned surfaces bioinspired from butterfly wings and lotus leaves is presented. Silica-based sol–gel films are thermally imprinted from elastomeric molds to produce stable structures with superhydrophobicity values as high as 160° water contact angle. The biomimetic surfaces are demonstrated to be tuned from superhydrophobic to superhydrophilic by annealing between 200 °C and 500 °C.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nature offers a variety of surfaces with functional properties and is a source of inspiration for numerous applications and technologies. Recently, it has been demonstrated that some biological surfaces are structured at the micro and nanometric scale as regards different properties such as superhydrophobicity or superhydrophilicity [1, 2]. More broadly, researchers are focusing on biological systems to create a surface with new functionalities; this field is popularly known as 'biomimetics' [3]. Well-known applications are lotus leaves and butterfly wings with their specific structure giving them superhydrophobicity or self-cleaning properties [4–6]. Several studies report both the understanding of these micro and nano-structures and the fabrication of biomimetic structures. One of the challenges is to replicate these biomimetic structures over large scales and at an affordable price for industrial applications such as, for example, the next generation of windows or windshields. Nanoimprint lithography is one of the most promising techniques due to its low cost, high throughput and ability to imprint large areas. Nevertheless, this procedure usually requires the fabrication of master-molds by conventional microelectronics techniques (lithography, etching, etc) which is time consuming and limits their sizes. In the present strategy, we use natural master-molds for casting elastomeric templates which thus simplifies their fabrication and allows us potentially to achieve original patterns which are difficult to fabricate. Few previous works report on the replication of the lotus leaf on elastomer materials such as polydimethylsiloxane [7] and polymers [8]. Here, we propose the next step with the replication of biomimetic surfaces on attractive silica sol–gel films by thermal nanoimprinting. Silica sol–gel materials have the advantage of being stable thermally, mechanically and chemically and they are used in many applications such as coating of glazing, optic materials, microelectronics and biomaterials [9, 10]. To use these advantages, we show the imprint of inorganically cross-linked silica sol–gels with features bioinspired from lotus leaves and butterfly wings. This paper describes a simple method for fabricating biomimetic and superhydrophobic surfaces which are thermally and mechanically stable.

2. Experimental details

The replication of the surface of a lotus leaf and a butterfly wing (*Papilionae Ulysse*) was carried out using a flexible polydimethylsiloxane (PDMS) template imprinted into a

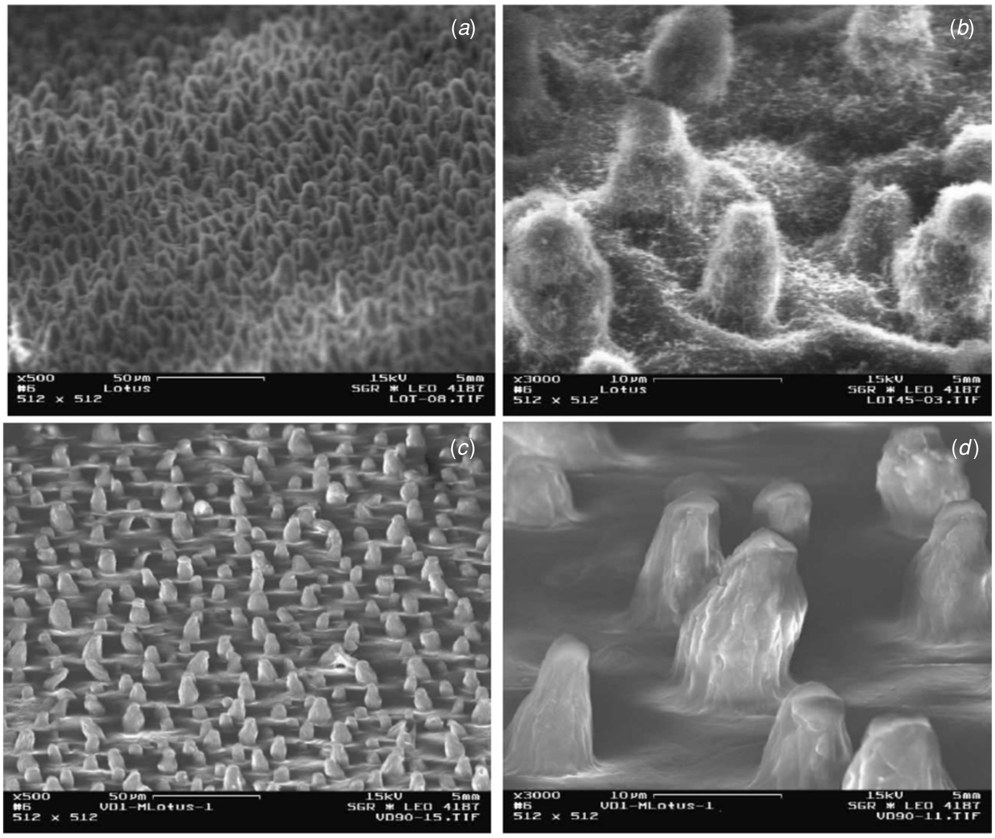

Figure 1. SEM images of the natural lotus leaf (*a*) and (*b*) and the replicated surface (*c*) and (*d*). Angle of view: 75° except for (*b*) 45°. The scale bar corresponds to 50 μm on (*a*), (*c*) and to 10 μm on (*b*), (*d*).

liquid sol–gel film. Elastomer PDMS templates were prepared by casting a liquid PDMS solution against the surface of the lotus leaf and the butterfly wing. After solidification at 80 °C for several hours, the PDMS layer was peeled off, resulting in a negative structure of the original template. In the case of a lotus leaf, the release from the mold was done easily, whereas the scales of the butterfly remained stuck to the PDMS. The butterfly wings being symmetrical, the PDMS mold can be used for the nanoimprint. Due to the low Young modulus of the PDMS (around 0.8 MPa), our templates can follow the curvature of natural leaves or wings and can be used to imprint spin-coated resist films at low pressures. Sol–gel resists are prepared from the methyltriethoxysilane (MTEOS) sol mixed in an aqueous solution under acidic conditions (pH = 3.1). A high MTEOS/H_2O (1:14) molar ratio is used to ensure a total hydrolysis of alkoxy-silane groups before imprinting. The solutions are stirred for one day at room temperature before use. MTEOS sol–gel films are deposited by spin coating on glass or silicon substrates. The MTEOS film thickness was approximately 900 nm as measured by a profilometer. The imprint pressure was kept lower than 2 bars and imprint temperature was kept between 80 °C and 150 °C for about 20 min. All imprints are done with the same two molds (lotus and butterfly) on typical surfaces from 4 cm^2 to 10 cm^2 with good homogeneity along the surface and reproducibility demonstrated for at least ten successive imprints of each template. Final annealing is performed between a temperature of 200 °C and 500 °C for 2 h to ensure a homogeneous and stable vitrification of our sol–gel films. For samples with the highest thermal treatment (500 °C), a surface grafting of fluoroalkylsilane was performed by evaporation for 12 h at 80 °C. All hydrophobic surfaces were characterized by their water contact angle with a droplet of 1 μL on a 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 of the lotus leaf with micrometer-scale pillars of 3–11 μm diameter and 7–13 μm height randomly covered by branch-like nanostructures of about 100 nm diameter (see figures 1(*a*) and (*b*)). We measured the density for these nanopillars around 3×10^{11} pillars per square meter from SEM images. As expected, the contact angle for these structures is measured around 160°, confirming superhydrophobic behavior and low surface energy. Only waxes have been cast into PDMS molds due to variable directions of nanobranches which cannot be turned out (figures 1(*b*), (*d*)). It is also interesting that the cover scales of most of the butterfly *Papilio* species (figure 2(*a*)) present a common bulk and surface structure. The upper membrane is constituted by a multilayered air/chitin film of about five to ten periods (figure 3) and the surface between the two ridges is periodically undulated, forming a regular set of concave cavities (figure 2(*b*)). According to the species, these cavities

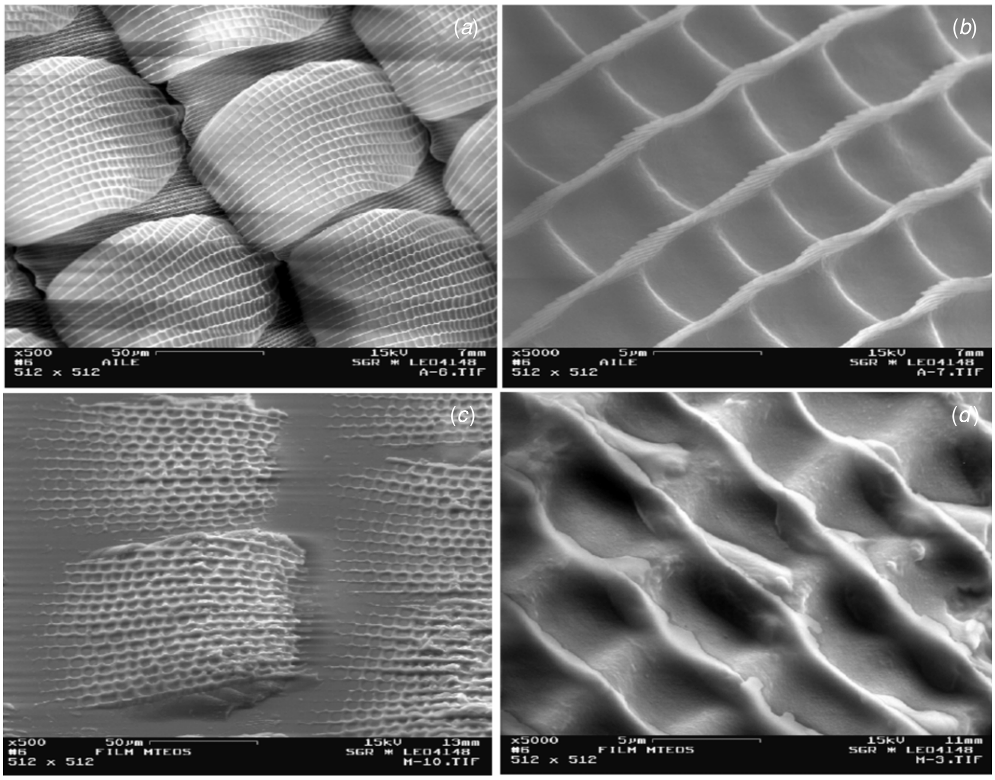

Figure 2. SEM images of the butterfly wing (*a*) and (*b*) and the replicated surface (*c*) and (*d*). Angle of view: 45°. The scale bar corresponds to 50 μm on (*a*), (*c*) and to 5 μm on (*b*), (*d*).

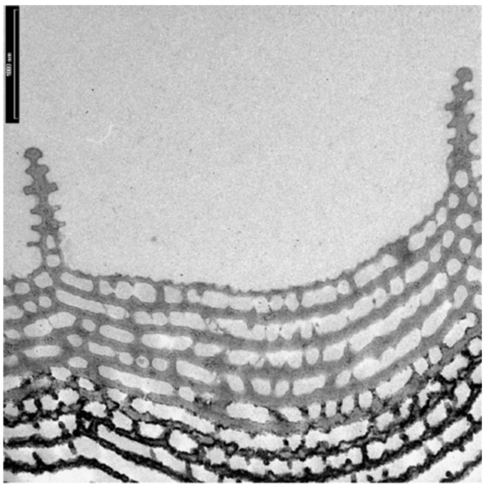

Figure 3. TEM view of a section of the individual cover scale. The scale bar corresponds to 1 μm.

are roughly spherical (*Papilio blumei* Boisduval, 1836) or slightly elongated (*Papilio peranthus* Fabricius, 1787). In our case, we investigate *Papilionae Ulysse* species for convex scales, each approximately 100 μm long (figure 2(*a*)). One scale is composed of both longitudinal ridges spaced 5 μm apart and cross-ribs of 3–6 μm (figure 2(*b*)). The surface of these scales is undulated and forms reservoirs between each cross rib [4, 5]. It is also found that a superhydrophobic surface for butterfly wings with a contact angle of about 160° is close to the value for the lotus.

Replication of surface morphology for both leaves and wings is depicted in SEM pictures 1(*c*), 1(*d*) and 2(*c*), 2(*d*) respectively. Micropillars of the lotus leaf have been fairly well imprinted with fidelity according to their size and direction but with lower pillar density than the original structures. It is found that only 50% of waxes are imprinted due to a low thickness of MTEOS films introducing a lack of matter to fill out the PDMS mold. In the same way, the scales of the butterfly wing are successfully imprinted with its ribs and cross ribs on each scale (figure 2(*d*)). Again, too low a thickness for MTEOS films coupled with the convexity of scales leads to a partial filling of the imprint mold and an inhomogeneous imprint along a scale (figure 2(*c*)). We observed that the filling and imprint of our sol–gel resist is deeper at the center than at the extremity of the scale and involves reservoirs and hollows with the plate bottom at the center and at the extremity, respectively, as shown in figure 4. One perspective on improving the quality of replication will be to increase the initial sol–gel layer to around 2 μm to fully fill out our imprint stamps.

Hydrophobic behavior for bioinspired surfaces is characterized by their static water contact angle. When compared to the water contact angle on uncoated glass of $39 \pm 1°$ and on MTEOS thin film of $86 \pm 2°$, it was found that the replicated surfaces showed higher values, with the same values of around $123 \pm 2°$ for lotus and butterfly replications (figure 5). This 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 with methyl groups on their

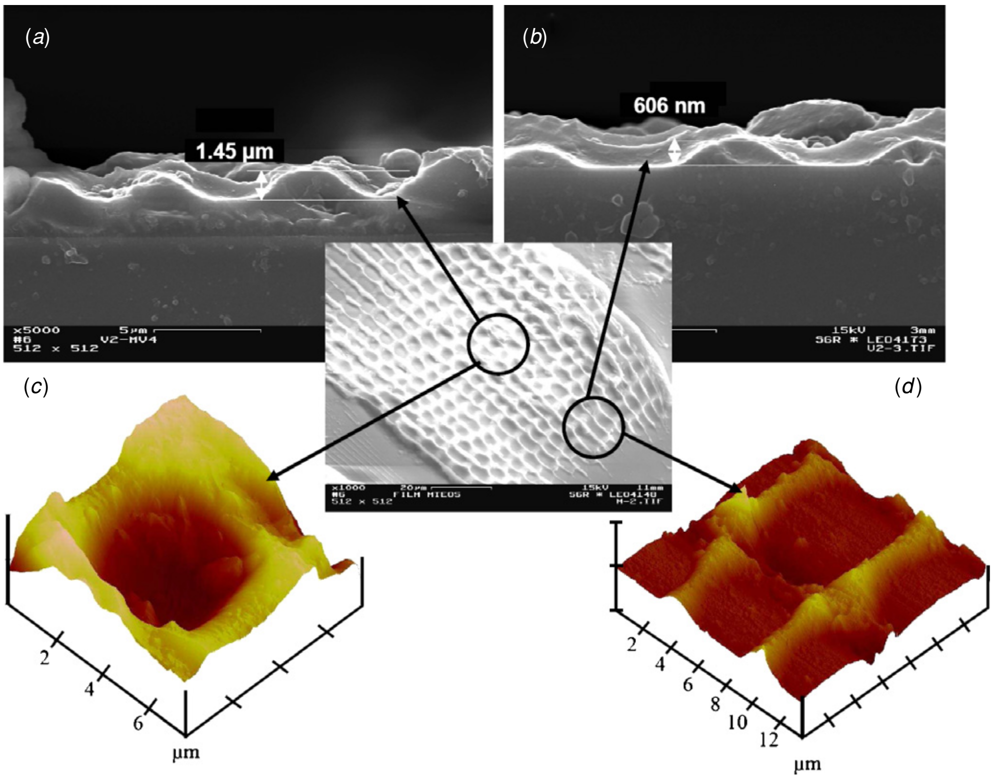

Figure 4. SEM and AFM images of the center (*a*) and (*c*) and of the extremity (*b*) and (*d*) of one imprinted scale in MTEOS films.

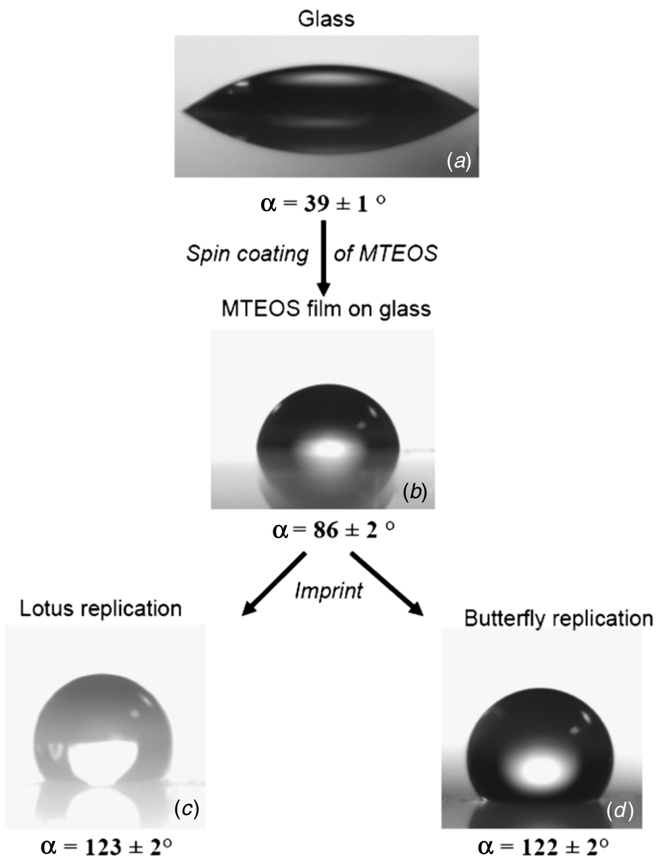

Figure 5. Side profile of a droplet of water on glass (*a*), MTEOS film coated on glass (*b*), replicated surface of the lotus (*c*) and of the butterfly (*d*).

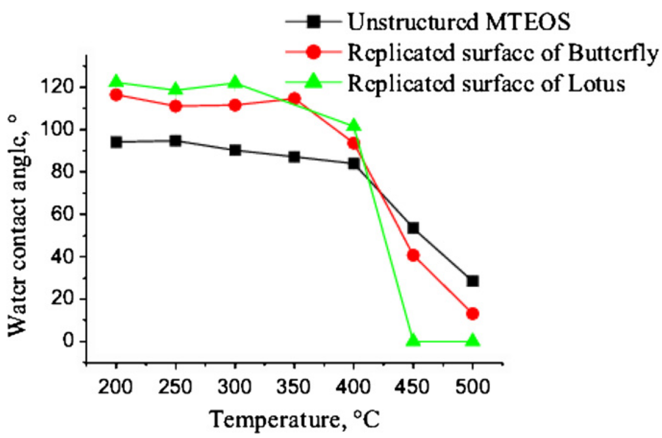

Figure 6. Water contact angle measurements on unstructured MTEOS (■), replicated surface of the butterfly (●) and replicated surface of the lotus (▲) as a function of heat temperature.

surface. These organic groups can be removed by annealing at temperatures higher than 450 °C [12]. A transition between the hydrophobic and hydrophilic surfaces is thus expected around 400 °C where the methyl groups are burnt. In the case of imprinted structures, the hydrophobicity is accentuated at low annealing temperatures and conversely the hydrophilicity increases at higher temperatures. We have observed this transition 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

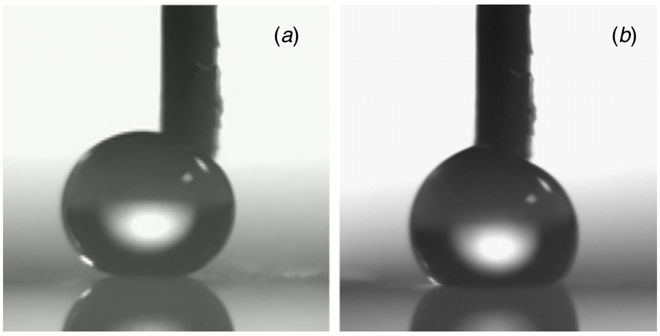

Figure 7. Syringe with water droplet on replicated surface of the lotus with high pillar density (*a*) and low pillar density (*b*).

pure silica structures after total burning of the 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 an average contact angle of about 120° for both lotus and butterfly replications. However, the water contact angle of the replicated structures is lower than 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°) for the lotus replication. Indeed, some areas of imprinted lotus samples are so superhydrophobic that it is not possible to deposit a water droplet on them (figure 7). The water droplets move to be on other areas where the pillar density is lower. For the butterfly replication, a homogenous imprint along the scale should lead to higher values of the contact angle. These results emphasize the importance of fabricating 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 the fabrication of superhydrophobic surfaces is reported by biomimetics of lotus leaves and butterfly wings. The specific behavior of imprinted silica sol–gel materials allows us to switch from superhydrophobic to superhydrophilic surfaces just by adequate annealing. These imprinted nano-structured films on silicon or glass substrates have the advantage of being stable up to high temperature with the formation of pure silica structures. The replicated structures can be covered by an adapted interferential multilayer that gives an iridescent color to the glass, without modifying its hydrophobic properties. These works should be investigated further.

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