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Controlling the wettability of polycarbonate substrates by producing hierarchical structures using Direct Laser Interference Patterning

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ABSTRACT

New strategies for the fabrication of surface structures using Direct Laser Interference Patterning are presented in this work, aiming to fabricate hierarchical structures with selective wetting properties. Polycarbonate sheets have been structured employing a two-beam interference arrangement using an ultraviolet (263 nm) nanosecond-pulsed laser, creating line- and pillar-like structures with simple and hierarchical geometries. Two different methods for producing hierarchical structures are here provided, both relying on a pixel-wise structuring technique and able to achieve high structure depths. The produced surface patterns are characterized by confocal microscopy, scanning electron microscopy and the influence of the surface topography on the water contact angle is investigated. The correlation between structure geometry and wettability response, in terms of structure height and directionality of the droplet shape is reported.

1. Introduction

In the last years, many efforts have been done in order to fabricate more and more functional surfaces with an increasing number of application cases. As our experience reveals, the first producer of smart surfaces is Nature, with a huge number of examples of structured surfaces observed in the vegetal and the animal world. For example, the superhydrophobic and self-cleaning properties of the lotus leaf have been ascribed to the micro- and nano-structure of the leaf texture [1], while the gecko's feet has hierarchical structures which permit to adhere on almost every surface [2] and the Collembola insect showed impressive anti-bacterial properties due to the hierarchical structures on the top of its skin [3,4]. Furthermore, the anisotropic wettability, i.e. the possibility to control the spreading of liquids on a determined direction, has recently gained interest especially in the microfluidics sector [5]. Natural examples of anisotropic wetting can be found in the rice leaf or in the butterfly wings, where the unidirectional micro-grooves are able to shed water along the longitudinal direction of the structures [6,7]. Since the discovery of water-repellence, fabrication techniques, models and analytical methods have been employed in order to reproduce the features that conferee to a material's surface the water repellence property. Although several examples of structured materials with simple and hierarchical structures have been realized, not all the processing techniques are capable of bringing smart materials in the everyday life environment.

In this work, we explore the possibility for new ways to microstructure materials employing Direct Laser Interference Patterning (DLIP) in order to fabricate hierarchical structures with distinctive anisotropic wetting properties. The wettability of the processed surfaces, in some cases strongly anisotropic, showed a high dependency on texturing geometry and depth.

1.1. Wettability change on structured surfaces

Within the natural examples for textured surfaces, the lotus leaf (Nelumbo nucifera) has deserved a special place in the collective understanding, since its combination of surface chemistry and micro-nanostructures are able to completely repel water droplets and, therefore, have even a self-cleaning character [1,8]. The tendency for a flat surface to attract or repel water droplet can be described through the Young's theory and the water contact angle (WCA) value [9]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos(\theta_Y) \tag{1}$$

where γ_{SV}, γ_{SL} and γ_{LV} are the solid-vapor, solid-liquid and liquid-vapor surface tensions, respectively, and θ_Y is the contact angle for a flat surface. Thus the balance between the surface tensions determines the WCA.

WCA values greater than 90° are associable to a hydrophobic surface, while values smaller than 90° are the result of wetting a hydrophilic surface. The Young's theory is however based only on the

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chemical “affinity” between water and the molecules at the surface, but as for the lotus leaf, the water repellence is mainly enhanced by the micro/nano-roughness of its features. The control of wettability through the roughness change has been then explained by two well-established theories, the Wenzel and Cassie-Baxter models, which describe a “wet” and “non-wet” contact between droplet and the structured surface, respectively.

The Wenzel model describes the variation of water contact angle θ according to Eq. (2), through a roughness parameter r_W defined as the ratio between the solid-liquid contact line (the perimeter of whole structure) and its projected area [10]:

$$\cos(\theta) = r_W \cos(\theta_Y) \tag{2}$$

As a result from the Wenzel model, an originally hydrophilic surface becomes more hydrophilic when the roughness of the surface is increased, while the hydrophobic character increases when the starting surface is already hydrophobic. On the other hand, the Cassie-Baxter model treats the wettability variation with surface roughness through Eq. (3):

$$\cos(\theta) = r_{CB}(1 + \cos(\theta_Y))-1 \tag{3}$$

where r_{CB} is a roughness parameter based on the ratio between the solid-liquid contact line and its projected area [11].

The Cassie-Baxter model is based on the assumption that the surface features are able to keep air pockets once the liquid droplet lays on the surface and therefore, the solid-liquid contact line is less than the structure perimeter. As a result of the Cassie-Baxter equation, the increase of the roughness results in an improvement of the hydrophobic character of the surface, both for an already hydrophobic or hydrophilic flat surface. As a summary for both models, when the roughness of a hydrophobic surface is increasing, the hydrophobic character is enhanced, which can lead to a super-hydrophobic state (WCA > 160°).

An important result of the two wettability models is related to the anisotropic spreading of a liquid droplet, in presence of highly oriented structures (e.g. lines). As reported in several experimental works and simulations, as long as a water droplet is in contact with the structured surface (Wenzel state), a strong relation between the structuring direction and the droplet spreading can be observed [6,12–16]. In particular, the droplet will tend to spread (lower WCA) in the direction parallel to the main texture due to capillary forces, while it contracts (higher WCA) perpendicularly to the main texture direction [13]. On the other hand, when the Cassie-Baxter state is granted, the water droplet is suspended on the surface through air pockets and therefore it is no more in contact with the structures. As a consequence the water droplet can experience no surface structure and no capillary forces tend to deform the droplet from the spherical shape.

1.2. Direct Laser Interference Pattering

Several manufacturing techniques have been employed to texture materials for changing their wettability and, in the last years, diverse procedures have been applied in order to mimic and create defined hierarchical structures. As described in the previous section, the wettability change can take place due to a change in the surface chemistry or due to a change in the roughness of the surface. In order to create deterministic structures, several techniques are nowadays available even with resolution up to the nanometer range and, among the mask-free fabrication methods, the laser structuring techniques have achieved an important role in the scientific community. Conventional laser fabrication techniques, as Direct Laser Writing (DLW) have been intensively used for the production of functional structures both on metals and polymers using ultra-short laser pulses [17–22]. Although the fabrication speed, by means of scanning devices, can be industry-appealing the technique presents clear limitations in feature resolution, due to the achievable beam spot size.

Another approach, known to be used to create structures much smaller than DLW, consists in employing ultra-short laser pulses and scanning repeatedly the surfaces. The structures, called Laser Induced Periodic Surface Structure (LIPSS) are created from diverse phenomena [23] which can be considered for the formation of ripples [24] micro-grooves and conical spikes [25]. The structure dimensions can be in the range of the laser wavelength (or below) and can be controlled through polarization, laser fluence and scanning speed [26]. Although the possibility to create hydrophobic surfaces [27], enhance the cell growth [28] and decrease the friction coefficient [29] have been demonstrated, the processing of LIPSS is strongly material-dependent and the creation of deterministic periodic structures cannot be granted.

A novel technique, Direct Laser Interference Patterning (DLIP), relies on the coherent overlap of two or more laser beams in order to treat the materials surface, by the generation of an interference pattern. The DLIP technique has demonstrated to be capable to process a wide number of material, ranging from metals to polymers and coated surfaces [30–36]. This technology has not only shown an enormous flexibility in creating surface structures with different pitches and geometries, but also high processing speeds (throughput) being capable to treat large areas [37–40]. Depending on the laser wavelength and the thermal and optical properties of the material, the structuring process can be driven by local ablation and/or melting, as well as other processes like swelling (as demonstrated on polymers or some coatings) [35,41–45]. The application fields for DLIP are related to friction reduction on metals, improved cell adhesion for dental implants, fabrication of nanoparticles for photocatalysis enhancement, growth of ZnO nanowires for sensing applications and wettability change on metals and polymers between others [34,46–49].

While the geometry of an interference pattern can be perfectly controlled by defining the number of the interfering laser beams, their geometrical arrangement, individual angle of incidence and phase and polarization, the characteristic pitch (spatial period, Λ) can be controlled through the variation of the intercepting angle between the beams. This is described in Eq. (4) for a two-beam DLIP setup:

$$\Lambda = \frac{\lambda}{2\sin(\alpha)} \tag{4}$$

where 2α denotes the angle between the interfering beams.

A possible processing strategy in DLIP is to employ a pixel-wise structuring, that means making use of slightly focalized interfering beams and irradiating areas with an interference area with dimensions ranging from tens to a few hundreds of μm (Fig. 1a) [40,45,50,51]. The pixel-wise structuring is also common in the DLW, where the combination of highly focalized beams, successive scans or multiple irradiations allows producing complex microstructures or higher aspect ratios [17,52,53]. Also in a previous work, it has been demonstrated that under specific conditions polymers can be structured by DLIP obtaining unusual ablation profiles [45]. This is the case of the transparent polycarbonate employed in this work which, for low special periods and high laser fluence, presents a high amount of unselectively ablated material in the upper part of the treated DLIP pixel volume. This unselective Gaussian ablation has been mainly ascribed to the relationship between plasma formation and the structure aspect-ratio, which means that high structures as well as close structures can be erased at the upper part of the surface due to the plasma formation and expansion, leaving a non-structured hole with a structured bottom (Fig. 1b). For some applications this structuring behavior could be considered as an imperfection, since most of the treated volume goes lost at the end of the process. However, in this paper we demonstrate how this phenomenon can be employed to obtain hierarchical structures.

Independently on the ablation process which the polymer undergoes, a conventional approach used to enhance the structure depth is to increase the laser fluence (laser energy density). Nevertheless, for high fluences saturation effects may arise, especially due to plasma shielding [54,55]. Therefore, in order to achieve structures with higher aspect ratios, an overlap between sequential laser pulses has been