BIO-INSPIRED LASER MICRO- AND NANOPATTERNING FOR FLUID TRANSPORT AND ANTI-ADHESIVE PROPERTIES

C. PLAMADEALA[1]*, G. BUCHBERGER[1], J. HEITZ[1], W. BAUMGARTNER[2]

[1]Institute of Applied Physics, Johannes Kepler University Linz, 4040, Linz, Austria
[2]Institute of Biomedical Mechatronics, Johannes Kepler University Linz, 4040, Linz, Austria
*cristina.plamadeala@jku.at

ABSTRACT

Bio-inspired micro- and nano-patterning of materials by means of laser radiation is a rapidly growing field for special industrial, medical, and scientific applications. This is significantly driven by the exciting properties of micro- and nano-patterned materials found in natural biological species, including wetting, directional fluid transport [1] and pronounced adhesive and anti-adhesive properties [2]. The structuring techniques addressed here focus on developments in laser processing using short and ultrashort laser pulses. This includes the self-organized formation of periodic micro- and nano-patterns at surfaces induced by exposure to laser radiation, as well as direct patterning techniques such as two-photon polymerization and UV lithography.

1. INTRODUCTION

Laser-induced periodic surface structures (LIPSS) are self-assembled micro- and nano-structures which can be generated by linearly polarized radiation on most materials. They allow the manipulation of important surface properties. As their fabrication is flexible, robust and mostly fast, LIPSS have found applications in fields of optics, fluidics, electronics, tribology, medicine etc. In this paper, we present an overview of our recent work, shortly covering the topic of bio-inspired LIPSS that can be used in directional fluid transport and adhesive and anti-adhesive surfaces applications.

2. MATERIALS AND METHODS

In this section we describe the setup used to produce all LIPSS presented in this paper, shown in **Fig. 1** and described in more details in [3]. The setup consists of a KrF* excimer laser (LPX 300, former Lambda Physik, now Coherent Deutschland GmbH, Germany), with a wavelength of 248 nm, and a pulse duration of 20 ns. The laser beam is linearly polarized with a α-BBO crystal (Melles Griot, Carlsbad, CA, USA), and projected onto the rotatable sample holder with the help of two fused silica lenses arranged in a telescope configuration. The sample is fixed on the sample holder with adhesive tape, and exposed to the KrF* laser beam under different angles of incidence, θ.

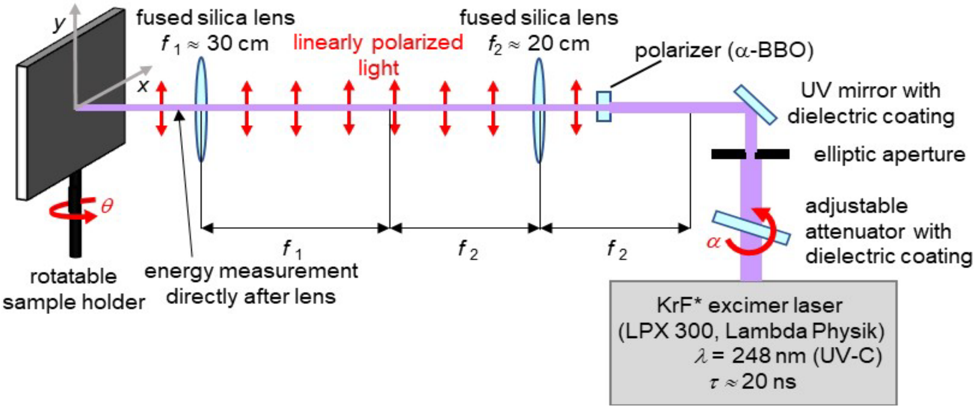

Fig. 1 Setup for LIPSS fabrication on polymer foils [4].

3. LIPSS FOR DIRECTIONAL FLUID TRANSPORT

In a biomimetic approach to imitate the wettability and directional fluid transport of the scent efferent system of true bugs [5], polyimide (PI) foils (UBE Industries, Ltd) were irradiated with the KrF* laser under a 45° incidence angle. This resulted in formation of tilted conical microstructures with a length of 25 µm and a width of 13 µm (**Fig. 2A** and **B**), comparable with the structures in the natural role model. To obtain a longer channel, the PI foil was horizontally moved at a speed of about 16.7 µm/s. The sample was exposed to 400 pulses, at repetition rate of 5 Hz, and with a fluence of 75 mJ/cm^2.

Wetting tests were performed to assess the wettability and eventual unidirectional fluid transport using a soap-water solution (with a contact angle of 35°, measured on non-processed PI foils) mixed with Ponceau Red dye (Sigma Aldrich, Germany). Samples were fixed at 45°, in such a manner that the tips of the cones point upwards. A 0.4 µL droplet of soap-water solution was applied in the middle of the structured area. It can be seen in **Fig. 2C**, that the liquid solution is moving upwards, against gravity, reaching the upper rim of the structured area, while the liquid front was halted in the downwards direction. These results show that it is possible to obtain an upwards directional liquid transport on a tilted surface, against gravity.

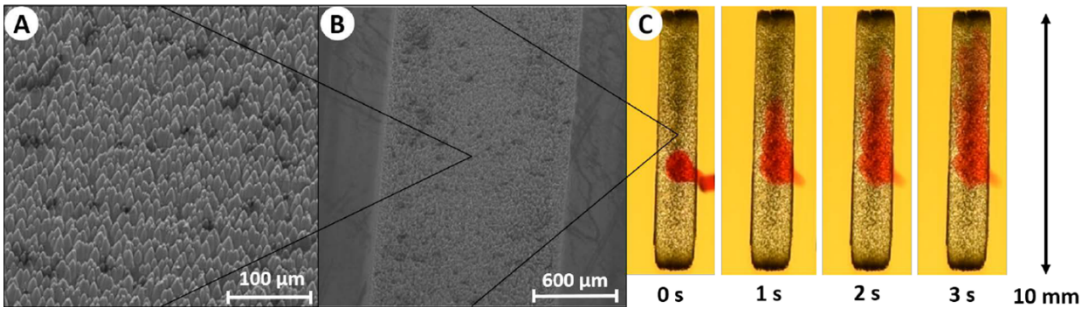

Fig. 2 Polyimide tilted conical structures. (A, B) Scanning electron microscope images (SEM) of the structures within the irradiated surface of the polyimide foil. (C) Directional liquid movement of the soap-water solution with a contact angle of 35° on an irradiated surface area of 10 mm × 1.5 mm, tilted at an angle of 45° starting from liquid deposition (0 s) and ending when the liquid has reached the upper rim of the structured area (3 s) [6].

4. LIPSS FOR ANTI-ADHESION APPLICATIONS

Cribellate spiders employ their *calamistrum* located on their hindmost legs (**Fig. 4A**), to process and assemble nanofibers into structurally complex capture threads [2]. A *calamistrum* (**Fig. 4B**) is a specialized comb, composed of fingerprint-like nanostructures. These structures hinder the nanofibers to adapt to the comb's surface, and therefore, reduce the contact area and the adhesive van der Waals forces between the nanofibers and the surface. Similar structures as found on the *calamistrum* can be produced on poly(ethylene terephthalate) (PET) foils (**Fig. 4C**) with a KrF* laser setup as described earlier. PET foils were irradiated under an incidence angle of 30°, with 6000 pulses, at a fluence of 10 mJ/cm^2, and a repetition rate of 10 Hz, resulting in a spatial period of the ripples of about 350 nm, and a ripple height of 100 nm.

Adhesion measurements were performed on structured and unstructured samples, as well as on their gold-coated counterparts (this step was performed to reduce the electrostatic forces). The samples were initially bent and brought into contact with the natural fibers, and afterwards - slowly and constantly drawn away from the thread until detachment. The measurements were video-recorded and the deflection of the nanofibers was measured and plotted as shown in **Fig. 4D**. It is clear that the gold-coated structured PET foil deflects the spider fibers the least, making it the least sticky surface. Also, it has been recently shown that the anti-adhesion depends on the ambient temperature and humidity [7]. As a technical application, structured surfaces could be used as collectors in electrospinning setups, making it easier to peel off the nonwoven nanofiber fabric.

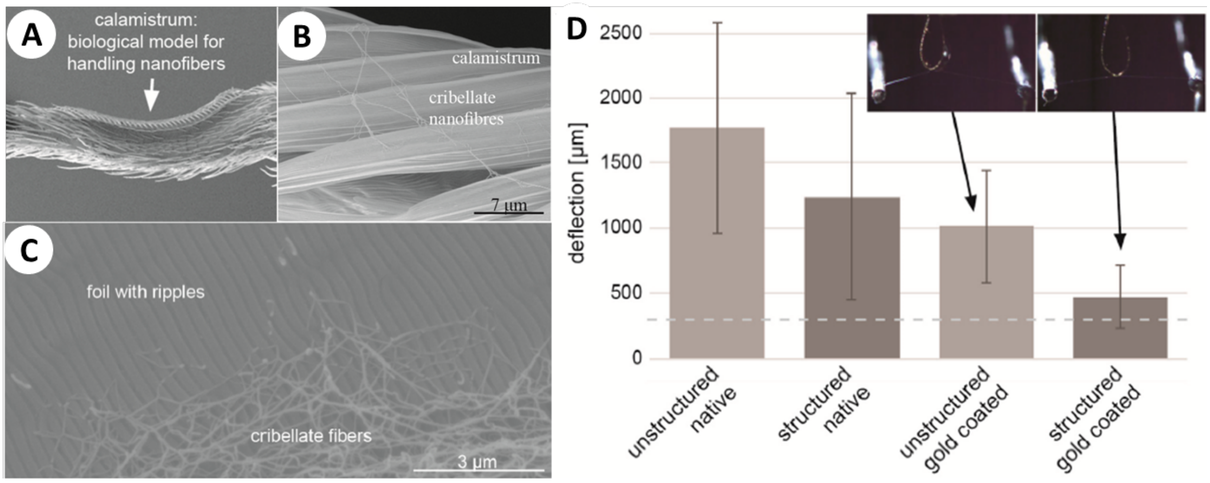

Fig. 3 (A) SEM of the metatarsus of the fourth leg of a cribellate spider, showing the depression where the *calamistrum* is situated as a specialized row of setae. (B) SEM close-up of single cribellate nanofibers placed artificially over the *calamistrum*. (C) Foil with nano-ripples as a biomimetic replication of the *calamistrum*, with artificially placed nanofibers on its surface. (D) Indirect measurement of the adhesive forces between the biomimetic foil by measuring the deflection of a 7-mm-long cribellate thread (insets: maximal deflection of the cribellate thread attached to a gold-coated structured foil and to an unstructured foil). The dashed line indicates the mean value of the data measured for the native *calamistrum*.

To mimic with a higher degree of exactness the *calamistrum's* hierarchical structures, i.e. micro-lines which are superimposed with nano-ripples (**Fig. 4A** and **B**), ultra-violet mask lithography was employed. Lines of 10 µm width, regularly distributed at 10 µm distance over an area of 3x3 cm² were fast and easily produced in SU-8 (Kayaku Advanced Materials, Inc.) (**Fig. 5A**). Further, the SU-8 lines were exposed to the KrF* laser beam, under different angles of incidence (3500 pulses at a fluence of 10-11 mJ/cm² and a repetition rate of 10 Hz). This resulted in nano-ripples with periods between 200 nm and 400 nm, and heights ranging between 60 nm and 100 nm. As this work is currently ongoing, peel-off measurements (as described in [8]) and adhesion measurements are in progress.

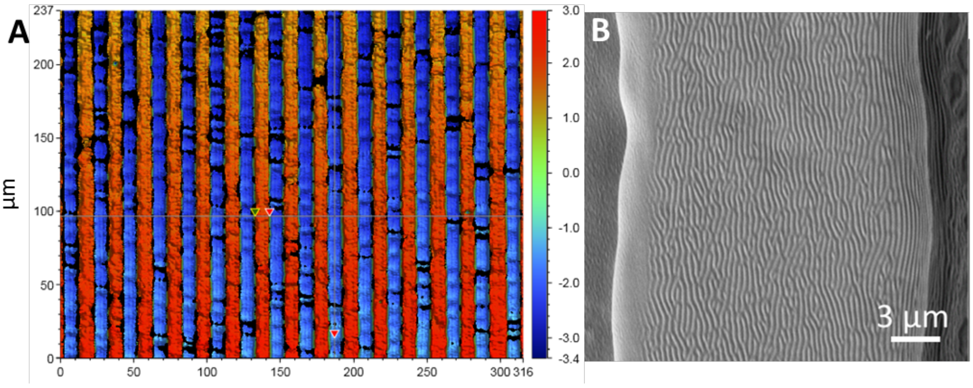

Fig. 4 (A) White light interferometry image of the lines produced in SU-8. (B) SEM of a SU-8 line which has been exposed to the KrF* laser at a 30° angle of incidence, showing nano-ripples with a spatial period of around 175 nm.

Considering that the nanofibers presented earlier are similar in diameter to the flagella and pili of bacteria, *Escherichia coli* (*E. coli*) TG1 bacteria were seeded onto PET samples (without ripples and with ripples of different spatial periods), to evaluate the effect of LIPSS on biofilm formation. To achieve nano-ripples of different spatial periods (ranging from approximately 200 nm to approximately 600 nm), the PET foils were exposed to the KrF* laser beam under six different angles of incidence (**Fig. 6A**) and with 6000 pulses at a repetition rate of 10 Hz using a fluence of 5.7-6.2 mJ/cm² [4]. When compared to non-irradiated surfaces (**Fig. 6B1**), laser-structuring of PET foils resulted in a significantly decreased cell adhesion (**Fig. 6B2-4)**. Spatial period plays a crucial role in bacterial adhesion – the smaller the spatial period is – the fewer cells attach to the nano-rippled surface: the strongest reduction in cell adhesion (~91%) was observed for periods of 214 nm (**Fig. 5C)**.

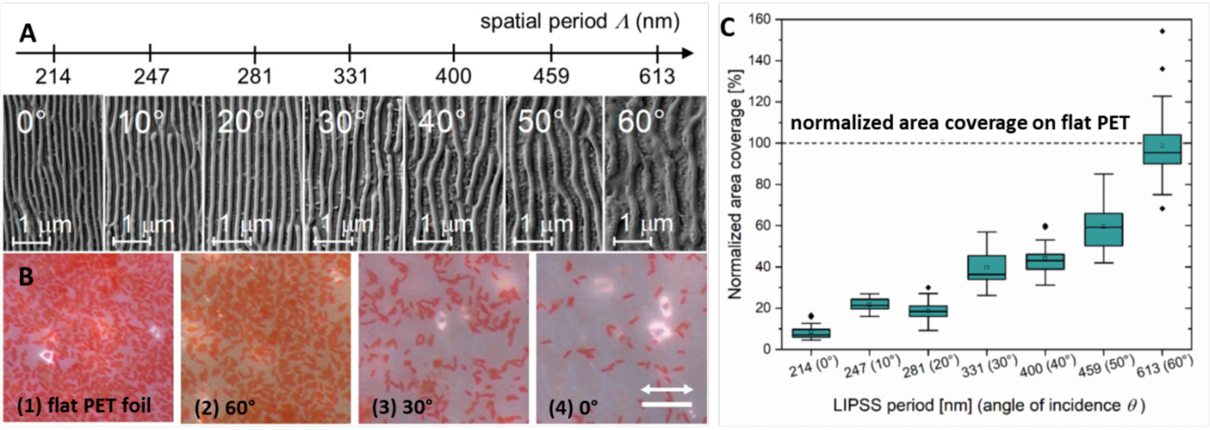

Fig. 5 (A) Nano-ripples with different spatial periods created by varying the laser beam incidence angle from 0° to 60°. (B) Optical reflected light microscopy of Safranine-stained *E. coli* TG1 on PET foils: (1) non-irradiated PET control sample; (2) laser-irradiated at $\theta = 60°$; (3) 30° and (4) 0°. Scale bar 10 µm. Arrow indicates LIPSS orientation in images (2-4). (C) Surface area of laser-irradiated PET covered by *E. coli* TG1 cells normalized against non-irradiated control surface.

ACKNOWLEDGEMENTS:

This study has received funding from the European Union's Horizon2020 research and innovation programme under grant agreement No 862016 (BioCombs4Nanofibers, http://biocombs4nanofibers.eu).

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