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# Water condensation enhancement over metallic hierarchical surfaces with controlled wettability fabricated by femtosecond laser

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## Abstract

The capability to enhance water condensation rate through the use of surfaces with controlled wettability, could dramatically improve technical applications ranging from the chemical to the power industry. Furthermore, any improvements in cycle efficiency would have a profound effect on important industrial areas such as power generation and water desalination. The rate of this phase change process is limited by how fast the droplets can depart the surface. For example, the condensation rate is significantly higher during condensation on hydrophobic surfaces, which promote formation of easily shedding droplets, than on hydrophilic surfaces promoting water film formation. Femtosecond laser machining is a robust, clean and scalable technique that can be used to manufacture surfaces with controlled wettability.

In this work, femtosecond laser ablation and LIPSS generation techniques were combined to fabricate surfaces with hierarchical roughness and extreme wetting properties in one step without the use of coatings or chemical treatments. Different patterns in the micro- and sub-micro-scale were fabricated and by changing the geometrical parameters different wetting properties were obtained. An experimental study of the droplet condensation rate and time to depart was performed over the fabricated surfaces with different contact angles.

Keywords: femtosecond laser; hierarchical roughness; condensation; wettability control

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## 1. Introduction

Femtosecond laser micro-nano machining has emerged as an effective technique to create dual scaled surfaces with nano- and micro-structure (Rukosuyev et al., 2014; Vorobyev and Guo, 2015; Zhang et al., 2016). These hierarchical structures are able to reproduce natural surfaces with extreme wetting properties such as the lotus surface (Bhushan, 2009) or the rose petal (Cao et al., 2015). Nature examples like these ones present patterns in the micro- and nano-scale which give them these special wetting properties. So, the goal is to achieve wetting properties similar to the ones present in nature by mimicking their surface morphologies with femtosecond laser texturing which is a robust, clean and scalable technique.

This wettability control of material surfaces has attracted a lot of interest in recent years because of its importance and applicability in fundamental research and practical applications such as self-cleaning ability (Bhushan et al., 2009), corrosion resistance (Su and Yao, 2014), cell adhesion control (Ranella et al., 2010), or anti-icing properties (Liu et al., 2015). Among all these applications, one of particular interest is the possibility of control the condensation rate over metallic surfaces thanks to the control of its wetting properties.

Droplet condensation occurs in many applications, for example, droplet condensation occurs in the early stage of frosting before ice crystals appear and a superhydrophobic surface can reduce the droplet growth and delay droplet solidification; therefore, the frost growth is reduced (Chu and Wu, 2016). In a condensation heat exchanger, if the material present superhydrophobic properties, the droplets will depart more easily and with a smaller departure diameter so the heat exchange surface is again exposed and the heat transfer is enhanced (Kruse et al., 2015). So, the capability to enhance water condensation rate through the use of surfaces with controlled wettability, could dramatically improve technical applications ranging from the chemical to the power industry. Furthermore, any improvements in cycle efficiency would have a profound effect on important industrial areas such as power generation and water desalination. The rate of this phase change process is limited by how fast the droplets can depart the surface. It has been demonstrated that in most cases, the condensation rate is significantly higher during condensation on hydrophobic surfaces, which promote formation of easily shedding droplets, than on hydrophilic surfaces promoting water film formation.

This work describes an easy fabrication method for metallic superhydrophobic surfaces based on femtosecond laser texturing, with no additional steps (avoiding the use of coatings or chemical treatments). First, micro-patterned structures were machined by means of laser ablation and after that, over the fabricated micro-patterns, nano-patterns based on LIPSS generation. This way, hierarchical structures combining patterns in the micro- and nano-scale were fabricated. The wetting properties have been analyzed and droplet condensation experiments were also performed on the fabricated surfaces to analyze the water condensation rate dependence on the surface wettability.

## 2. Materials and Methods

### 2.1. Materials and characterization

Austenitic stainless steel (AISI304) plates with a thickness of 0.5 mm were used. Before and after being treated by the laser the samples were cleaned in a 10 min ultrasonic acetone bath, followed by a 10 min ethanol bath. A 3D field-emission scanning electron microscope (FE-SEM) system supplied by FEI was used to study the topography. Contact angle measurements were obtained by gently dispensing a 3.5  $\mu$ l droplet of distilled water with a micro-syringe on each sample surface. The whole process was recorded with a digital camera. In order to measure the contact angle, the recorded videos were analyzed and the contact angle measured using the sessile drop method with the Low-Bond Axisymmetric Drop Shape Analysis (LBADSA)

plugin for ImageJ. Successive measurements were reproducible with an average error of  $\pm 2.5^\circ$ . All contact angles measurements were carried out at room temperature.

## 2.2. Femtosecond laser machining

Samples were machined in open air atmosphere with a Ti: Sapphire laser system consisting of a mode-locked oscillator and a regenerative amplifier which was used to generate 130 fs pulses at a central wavelength of 800 nm, with a 1 kHz repetition rate. The pulse energy was adjusted with a two-step setup: a variable attenuator formed by a half-wave plate and a low dispersion polarizer. The 8 mm diameter ( $1/e^2$ ) laser beam was focused on the samples using a 10x microscope objective with a NA of 0.3 to a beam diameter ( $\omega_0$ ) of approximately 6  $\mu\text{m}$ . This parameter is defined and standardized as the diameter at which the beam irradiance (intensity) has fallen to  $1/e^2$  (13.5%) of its peak (ISO 11146–2:2005). The fluence, or irradiance, was changed by adjusting the distance between the objective and the sample (moving the sample further away from the objective). The objective together with a CCD camera was used for online monitoring the structuring process. A three dimensional translational stage moved the sample under the beam at different speeds with sub-micron accuracy.

## 2.3. Condensation experiments

The condensation experiments were performed in a climatic chamber with controlled temperature and humidity. A Peltier Cell was used to force the sample temperature to reach the dew point and monitored with thermocouples. The selected conditions were a chamber temperature of 30°C, a humidity of 60 % and a sample temperature of 13°C.

# 3. Results

## 3.1. Femtosecond laser fabricated structures

Hierarchical structures with a dual scale roughness were successfully fabricated with a pitch distance (line separation) of 30  $\mu\text{m}$  in one and two dimensions and also covered by a LIPSS nanopattern. FE-SEM images of the final structures are shown in Fig. 1. The laser parameters selected in order to fabricate the micro- and nano-patterns were chosen based on previous works performed in the research group (Martínez-Calderon et al., 2016, 2015) and are detailed in this section.

The micro-patterns were fabricated with a pulse energy of 25  $\mu\text{J}$ , a scanning velocity of 1 mm/s and two overscans. These parameters lead to a Fluence of approximately 23  $\text{J}/\text{cm}^2$  and 15 pulses/spot, focusing the laser spot to a  $\omega_z$  of approximately 15  $\mu\text{m}$ . The resulting microstructures had a line width of 15  $\mu\text{m}$  and an ablated depth of 10  $\mu\text{m}$ .

The nano-patterns were fabricated with the objective of generate LSFL (Low Spatial Frequency LIPSS) nanopatterns which present a period of approximately 580 nm and a nano-depth of approximately 250 nm as it was characterized in (Martínez-Calderon et al., 2015). The selected parameters were a pulse energy of 16  $\mu\text{J}$  and a scanning velocity of 0.5 mm/s. These parameters lead to a Fluence of approximately 0.6  $\text{J}/\text{cm}^2$  and 170 pulses/spot, focusing the laser spot to a  $\omega_z$  of approximately 85  $\mu\text{m}$ . As it can be observed in Fig. 1c and d, the LSFL nanopattern was generated all over the micropatterned surface and in the non-ablated areas in a very homogeneous way, showing a representative micro/nanoscale binary structure.

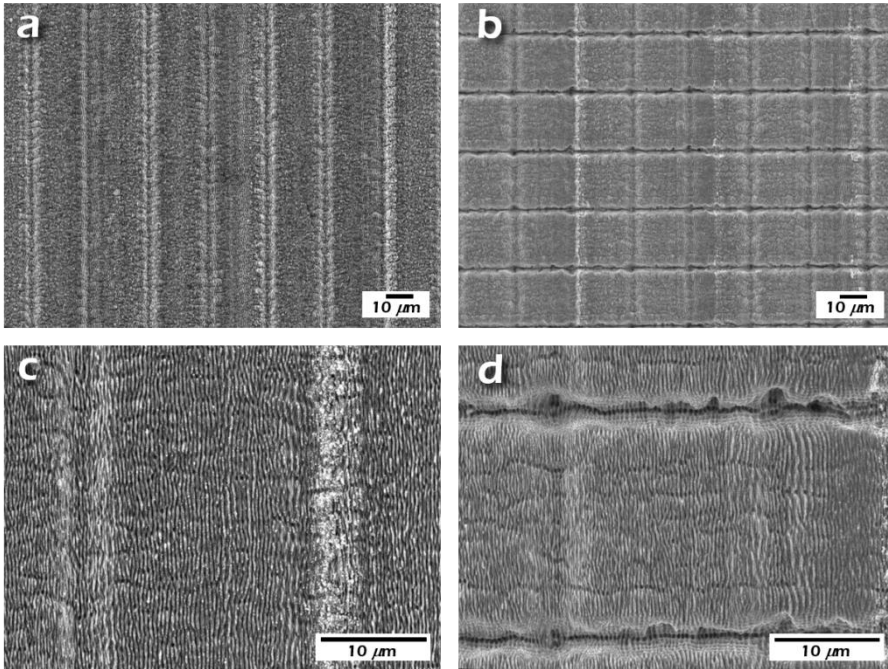


Fig. 1. FE-SEM images of the fabricated hierarchical structures: (a) 1D micropattern with a pitch distance of  $30\ \mu\text{m}$  covered by LIPSS (b) 2D micropattern with a pitch distance of  $30\ \mu\text{m}$  covered by LIPSS. Detailed area of the LIPSS nanopattern covering each micropatterned surface scanned on: (c) 1D micropattern (d) 2D micropattern.

### 3.2. Wettability behavior

Contact angle measurements were performed on the fabricated samples. Apart from the hierarchical structures previously described, another sample with only the LIPSS nanopattern was fabricated. The objective was to obtain different values of contact angle and compare the behavior in the condensation experiments that will be shown in the next section. The contact angle measurements are shown in Fig. 2 for the different performed surfaces. The hierarchical surfaces showed a superhydrophobic behavior having contact angles higher than  $150^\circ$  (Fig. 2a and 2b). The sample fabricated with only a LIPSS nanopattern showed a contact angle smaller being  $129^\circ$  (Fig. 2c). Finally, the non-treated surface showed a contact angle of  $79^\circ$  (Fig. 2d), being a hydrophilic surface. So we were able to obtain a good range of contact angles in order to study the water condensation dependence on this important parameter.

Fig.2. Droplet of  $3.5\ \mu\text{l}$  gently dispensed on the fabricated structures: (a) 1D micropattern covered by a LIPSS nanopattern (b) 2D micropattern covered by a LIPSS nanopattern (c) LIPSS nanopattern without micropattern (d) non-treated surface.

Fig.2. Droplet of  $3.5\ \mu\text{l}$  gently dispensed on the fabricated structures: (a) 1D micropattern covered by a LIPSS nanopattern (b) 2D micropattern covered by a LIPSS nanopattern (c) LIPSS nanopattern without micropattern (d) non-treated surface.

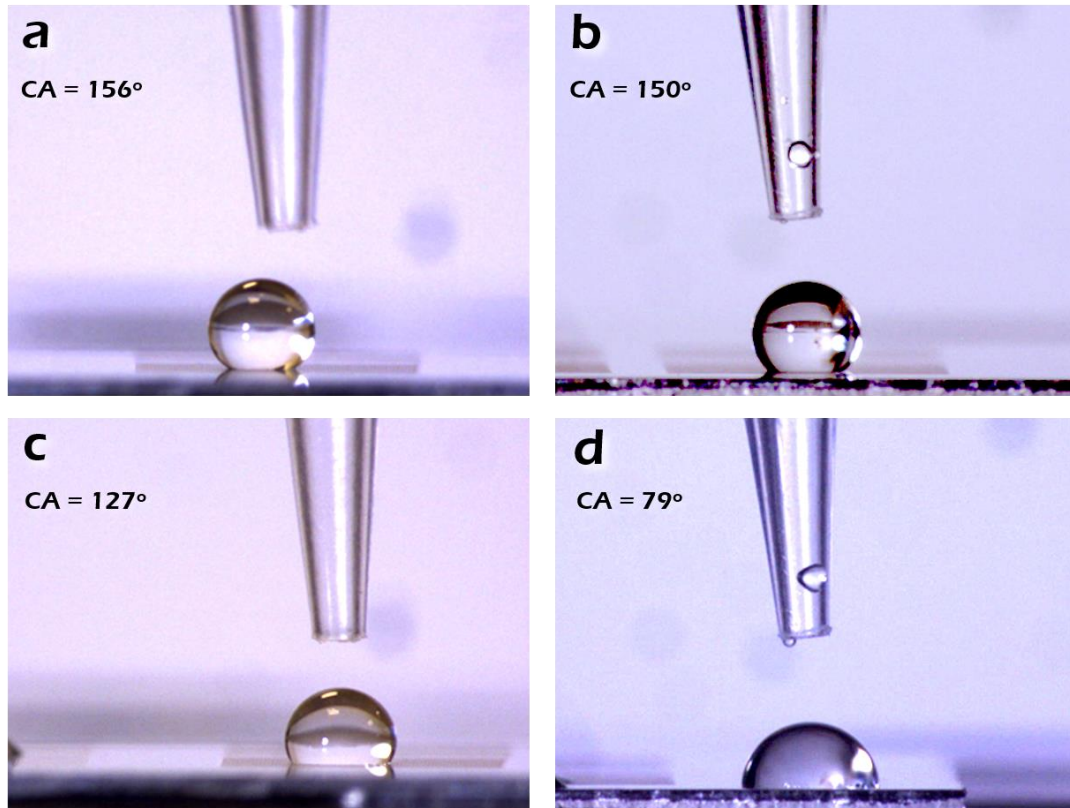


Fig. 2. Droplet of 3.5  $\mu\text{l}$  gently dispensed on the fabricated structures: (a) 1D micropattern covered by a LIPSS nanopattern (b) 2D micropattern covered by a LIPSS nanopattern (c) LIPSS nanopattern without micropattern (d) non-treated surface.

### 3.3. Condensation rate depending on the wetting properties

During condensation, the superhydrophobic surfaces presented a lower droplet density, the droplets showed much higher mobility and a greater diameter variation. The coalescence time was larger on the superhydrophobic surfaces. The surface fabricated with only the LIPSS nanopattern which present an intermediate wettability showed a behavior more similar to the superhydrophobic ones but the droplets mobility was slower.

Finally, the condensation rate was demonstrated to be much higher on the superhydrophobic steel surfaces than in the non-treated (hydrophilic) steel. So the femtosecond laser texturing was successfully used in order to improve this surface property.

## 4. Conclusions

In this work femtosecond laser texturing was used to successfully fabricate surfaces with different wetting properties. Surfaces with contact angles ranging from 80° up to 156° were fabricated only with the laser texturing step avoiding the use of coatings or chemical treatments which will make the process slower and harder to scale up to industry. The condensation rate was studied for each surface in order to analyze the

dependence on the wettability. It was found that the surfaces with larger contact angles show a lower droplet density, higher droplet mobility and greater diameter variation. Finally, the condensation rate was demonstrated to be much higher on the superhydrophobic steel surfaces than in the non-treated (hydrophilic) steel. So as a first approximation, femtosecond laser texturing was successfully used in order to improve this surface property.

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