Article

Superhydrophobic Surfaces Enabled by Femtosecond Fiber Laser-Written Nanostructures

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Abstract: Inspired by the self-cleaning and water-repellent lotus leaf, we have developed an efficient process to create superhydrophobic metal surfaces using a femtosecond fiber laser and have investigated the mechanisms of the structured metal surfaces in relation to their hydrophobicity. The at will feature of femtosecond fiber lasers can write versatile patterns of hydrophobicity with nanoscale precision on any metal. The results show that the homogeneously distributed hierarchical structures exhibit multifunctional properties, including superhydrophobicity, self-cleaning, and light-trapping. By optimizing the fabrication conditions, we have achieved a contact angle as high as 171° and a rolling angle of less than 3°. The structure is also resistant to an extreme temperature range of −40 °C to 71 °C and temperature shocks from 20 °C to −40 °C. This research highlights the exciting potential applications of superhydrophobic metals in the aviation, biomedical, and solar energy industries and beyond.

Keywords: ultrafast laser; femtosecond fiber laser; laser processing; hydrophobic surface; water repellent; surface nano-structuring

1. Introduction

Nature has created many living species with diverse wetting surfaces so that they can adapt to their habitats. Examples include self-cleaning lotus leaves [1] and rose petals [2], water-collecting Namib desert beetles [3], Morpho butterflies with unidirectional-wetting wings [4], etc. In 1997, Barthlott and Neinhuis revealed nature’s mystery for the first time and found that lotus leaves are comprised of randomly oriented papillose epidermal cells covered with hydrophobic epicuticular wax [5].

Their findings stirred great interest in hydrophobicity research [6], and since then this area has attracted increasing attention due to its wide range of applications in the automobile, aerospace, naval, plumbing, and biomedical industries for functions such as hydrophobic surface corrosion resistance, rust prevention, friction reduction, and the improvement of cell adhesion [7–12]. In the hydrophobic realm, automobiles and aircraft can have self-cleaning and anti-frosting properties, and medical implants can prevent blood coagulation and reduce the incidence of diseases like stent thrombosis [10–12].

Four methods of creating hydrophobic surfaces are adopted in this current field: chemical etching [13], reactive-ion etching [14], lithography [15,16], and coating [17]. These processes alter the material surface to make it hydrophobic through reactions with acids and bases, the induction of plasma, exposure to radiation, or coatings involving chemicals. Although the processed surfaces can exhibit hydrophobic behavior, these techniques usually involve complicated fabrication processes and have many limitations, including the need for hazardous x-rays, chemicals, and multiple steps.
that reduce the yield. Moreover, they lack long-term durability and stability in terms of maintaining hydrophobic behavior and surface structures [18].

Laser irradiation using pulsed lasers has been widely accepted as one of the next generation technologies as it involves a relatively simple process, has a potentially low operation cost, and avoids hazardous materials. In addition, the at will feature of the laser enables it to create any complex pattern on any material and surface morphology for a myriad of applications. Through well-controlled melting, ablation, and re-solidification, the laser writes nanostructures on top of microstructures on the material surface, producing robust hydrophobic hierarchical structures [19].

Current research on laser-based hydrophobic processes mainly uses femtosecond (fs) solid state lasers (e.g., Ti:sapphire). A group of scientists have applied this method to their research [20,21]. By utilizing the laser’s powerful pulses to produce microgrooves on the metal surface, they controlled the wetting properties of the metal and created a new surface that was highly absorptive, superhydrophobic, and self-cleaning. Another group manufactured hierarchical structures with an fs laser [22]. They divided the process into two steps: first, a microscale ablation was produced on stainless steel at a high pulse energy and with different velocities; second, nanostructures were ablated on top of the micro-structures using laser-induced periodic surface structures (250 nm high and with a period of 600 nm) to create a hierarchical structure.

The results of these groups are promising but the processes are slow. Currently, it takes an hour to process a 1 × 1 inch area [23]. This is because the solid state Ti:Sapphire fs lasers usually have a low pulse repetition rate (PRR) of less than 10 kHz [24]. Moreover, these solid state lasers are hard to maintain and operate. All of these characteristics hinder the potential industrial applications of hydrophobic surfaces produced by fs solid state lasers.

In contrast, the fs fiber laser offers an emerging technology with unique features, such as its compact size (5x smaller), low price, low maintenance, high PRR (hundreds of kHz versus 10 kHz), high wall plug efficiency (30% versus 1%), and better beam quality. The technology has been quickly adopted in both research and industrial fields [25]. It is of great interest to apply fs fiber lasers to hydrophobic metal processing.

In this paper, we report our study of developing a process to create superhydrophobic metal surfaces using a high energy fs fiber laser and investigating the structured metal surfaces in relation to hydrophobicity.

2. Materials & Methods

2.1. Materials and Conditions

All experiments were conducted in ambient air at 21 °C with a constant air flow running across the metal surface during the experiment to flush out the plume of ablated and recondensed material into an exhaust hood. Stainless steel (304) plates (10 mm thick) were used for all experiments. Samples were polished and carefully cleaned by an ultrasonic cleaner filled with isopropanol prior to the laser processing.

2.2. Laser System Setup

There are four parameters that play an especially important role in creating hierarchical structures: pulse repetition rate (PRR), energy per pulse, scanning speed, and pitch [26]. The experiment setup allowed these parameters to be adjusted for processing (Figure 1).

In the experiment, we used an fs fiber laser (Uranus 3000, Laser-Femto, San Jose, CA, USA), with a wavelength of 1030 nm. The pulse width was 750 fs and the maximum output energy per pulse was 100 µJ. The pulse energy was adjustable by an optical attenuator to obtain the desired energy level. An acousto-optic modulator (AOM, Gooch Housego, Ilminster, UK) was used to adjust the PRR from 100 kHz up to 1 MHz. The laser beam was guided by mirrors (Thorlab) towards an automated scanner (ScanLab, Puchheim, Germany) and focused by an F-theta lens (f = 100 mm, Thorlab, Newton, NJ, USA)
onto the sample. The sample was mounted on a computer-programmed 5D translation stage with nano-precision (AeroTech, Pittsburgh, PA, USA). As the motorized stage moved the metal sample in a linear direction, the scanner directed beams at a preset speed onto the sample. The sample was scanned line by line; the distance between each line is called pitch (hatch space).

![Figure 1](image_url)  
*Figure 1.* The schematic of the experiment setup for the fabrication of nanostructures on a metal surface. AOM: acoustic optical modulator. The devices in red text were assembled to allow for the adjustment of the process parameters.

A charge-coupled device (CCD) camera (Thorlab) was used to obtain a live view of the laser writing. The output collimated beam was a nearly symmetric Gaussian with $M^2 < 1.3$ (beam quality factor). A beam shaper (PiShaper, Berlin, Germany) was used to transform the Gaussian shape beam into a flat top shape so that a more uniform energy distribution could be achieved than the original round-shaped beam (Figure 1 inset). All the parameters were controlled by a computer, which signaled the laser to irradiate its beams accordingly. The setup was placed on a 4′ × 6′ optical table.

### 2.3. Characterization of Surface Structure

The morphology of the laser-structured surface was characterized by a scanning electron microscope (SEM, FEI QUANTA FEG 600). The surface morphology and wettability of laser-processed surfaces were evaluated as functions of PRR, laser pulse fluence (a ratio of laser pulse energy and beam area), scanning speed, and pitch.

To further characterize the surface morphology, the wavelength-dependent reflectance in the visible spectral range (i.e., 360–740 nm) was measured by a spectrophotometer (CM-2600d, Konica Minolta, Tokyo, Japan). The reflectance value was obtained for each experimental condition and correlated with the SEM measurements and the degree of hydrophobicity.

The hydrophobicity of the surface was evaluated by measuring the contact angle and the rolling angle of water droplets deposited on the structured metal surface. The contact angle is defined as the angle of a droplet where the water–air interface intersects the metal surface, characterizing the tendency of a liquid to spread on a solid surface; the rolling angle represents the inclination of a surface from which a drop rolls off. Superhydrophobicity is generally accepted as when the contact angle exceeds 150° and the rolling angle is less than 10° [27].

We used a method similar to the static sessile method and we captured the water droplet's contact with the metal surface using a high-resolution CCD and a macro-lens camera [28]. Then, we used image processing to calculate the contact angle as defined previously. To measure the rolling angle, we gradually tilted the substrate to determine when the droplet started to move.
3. Results and Discussion

We were successful in creating metal surfaces with uniform superhydrophobic properties using the fs fiber laser (Figure 2).

![Water droplets rolled to the edge of the sample, exhibiting uniform superhydrophobic properties across a 3 x 3 cm structured metal surface.](image)

**Figure 2.** Water droplets rolled to the edge of the sample, exhibiting uniform superhydrophobic properties across a 3 x 3 cm structured metal surface.

### 3.1. Effect of Laser Irradiation on Surface Morphology

During line-by-line processing (lines separated by the pitch), the laser both moves and removes material from the surface via metal melting and evaporation (ablation), thus forming periodic structures (re-solidification). To fabricate metals with hydrophobic properties, the surfaces must be made into one of the three structures: microstructures, nanostructures, or hierarchical structures [29]. Hierarchical structures are nanostructures formed on microstructures. Studies have shown that structures with higher aspect ratios resist water condensation better, exhibiting greater hydrophobicity [30].

SEM images were obtained for analysis of the structures of the fs laser-processed surfaces. Figure 3 displays the hierarchical structures, estimated to have an aspect ratio of 3, at different magnifications with a resolution from microscale to nanoscale. Coral-like surface structures with microcavities were formed at random orientations. These randomly oriented microcavities consisted of small grooves with dimensions in the range of 5–10 µm, which created an ultrafine porous structure. Further studies demonstrated that these structures were reproducible and were well-controlled by adjusting the laser parameters.

![The fabrication of homogeneous hierarchical structures on a metal surface that resulted in hydrophobic traits, presented with different resolutions of 100 µm (left) and 10 µm (right) scale bars.](image)

**Figure 3.** The fabrication of homogeneous hierarchical structures on a metal surface that resulted in hydrophobic traits, presented with different resolutions of 100 µm (left) and 10 µm (right) scale bars.

Although these structures were oriented randomly, when they formed a homogeneous pattern (Figure 3), the metal surface was found to be hydrophobic; when they formed a heterogeneous pattern (Figure 4), the surface was found to be hydrophilic. A possible explanation for this phenomenon is...
that suboptimal parameters generated non-uniform thermal conductivity, causing uneven ablation and re-solidification throughout the surface.

Figure 3. The fabrication of homogeneous hierarchical structures on a metal surface that resulted in hydrophobic traits, presented with different resolutions of 100 µm (left) and 10 µm (right) scale bars.

3.2. Effect of Laser Irradiation on Metal Wettability

As laid out in Section 2.2, a series of experiments were performed to optimize the laser and process parameters, which mainly included the PRR, pulse energy, scanning speed, and pitch. In the experiments, the PRR was first evaluated from 100 kHz to 1 MHz. Two groups of parameters resulted in the highest contact angles, demonstrating the most promising results. Therefore, our discussion will be mainly focused on these two groups:

1) the PRR of 100 kHz (energy: 8, 16, 32, 55 µJ; scanning speed: 50, 100, 200, 500, 800 mm/s; pitch: 2, 5, 7 µm), and
2) the PRR of 200 kHz (energy: 8, 16, 32, 55 µJ; scanning speed: 50, 100, 200, 500, 800 mm/s; pitch: 2, 5, 7 µm).

Figure 5 plots the resulting contact angles for various pulse fluences and scanning speeds, shown on the left and right, respectively. Only one variable was adjusted for each set of measurements. From Figure 5, it is evident that when the pulse fluence increased from 0.5 to 2 J/cm², the contact angle increased with the pulse fluence and reached the maximum value at the fluence of 2 J/cm². The further increase in the pulse fluence to 20 J/cm² caused a reduction in the contact angle. This was because the ablation-dominated process where excess fluence was present removed too much material from the surface before re-solidification [31]. A similar trend can be observed for the scanning speed. The maximum contact angle was reached at the scanning speed of 100 mm/s. The further increase in the scanning speed caused the ablation to be less effective. These results indicate that a balance between material ablation and re-solidification is critical in creating the desired hydrophobic surface.

Later in the study, the pitch dependence on hydrophobic performance was also investigated. Interestingly, it was found that the pitch had a more pronounced impact on the hydrophobic properties than the other parameters, as shown in Figure 6. With the other parameters kept constant, a pitch of 5–6 µm exhibited the best hydrophobic properties (166° contact angle and 3° rolling angle). Pitches that were too narrow (e.g., 2 µm) caused too much beam overlap between the two adjacent scanning lines, which led to a diminishing of randomly oriented structures. In contrast, too wide of a pitch (e.g., 8 µm) left some areas less processed or completely unprocessed.
When water droplets encounter the surface of the lotus leaf, they simply bead up and roll off. Studies have shown that the surface of the lotus leaf has a hierarchical structure, which exhibits a Cassie–Baxter state [32]. Water in the Cassie–Baxter state is suspended on the top of the surface, creating air pockets between the solid nanostructures, resulting in a water-repellent surface. Dirt particles on the surface stick to the droplets due to the natural adhesion between water and solids as well as the significantly reduced contact area between the water and leaf.

3.3. Water-Repellent and Self-Cleaning Properties

The initial concept of ultra-hydrophobicity was inspired by the lotus leaves of Nelumbo [1]. When water droplets encounter the surface of the lotus leaf, they simply bead up and roll off. Studies have shown that the surface of the lotus leaf has a hierarchical structure, which exhibits a Cassie–Baxter state [32]. Water in the Cassie–Baxter state is suspended on the top of the surface, creating air pockets between the solid nanostructures, resulting in a water-repellent surface. Dirt particles on the surface stick to the droplets due to the natural adhesion between water and solids as well as the significantly reduced contact area between the water and leaf.

Figure 7 depicts water-repellent characteristics through a series of frames extracted from a video clip over the course of eight seconds. The water droplets, upon contact with the laser-textured surface, immediately bounce off. The self-cleaning characteristic is also demonstrated. From a nine second video clip, Figure 8 shows how water droplets can quickly clean up debris by tilting the surface at a 3° angle.
3.4. Light-Trapping Effect

Another important finding is the inverse correlation of hydrophobicity with the reflectance of structured metal surfaces. Hierarchical structures with presumably higher aspect ratios absorb light more efficiently, producing darker surfaces [31,33]. In our study, we discovered that surfaces with less reflectance tended to be more hydrophobic than ones with a higher reflectance (Figure 9). Therefore, the level of reflectance would serve as a quick indicator of hierarchical structure and consequently of hydrophobicity.

Figure 7. A series of frames of water droplets bouncing off a hydrophobic metal surface fabricated by fs fiber lasers over a time interval of 7 s. (a) Water droplet exits the needle. (b) First water droplet makes contact with metal. (c) First water droplet rolls off the hydrophobic region of the metal. (d) Second water droplet drops on the metal surface. (e) A third water droplet makes contact with the second water droplet still on the hydrophobic region of the metal. (f) The second and third water droplets roll off the processed area and merge with the first water droplet.

Figure 8. A series of frames of water droplets cleaning aluminum oxide powder on the hydrophobic metal surface over a time interval of 8 seconds. (a) First water droplet makes contact with the powder and hydrophobic region of the metal. (b–e) As droplets move down the surface, the powder on the metal is collected. (f) The water droplet with the powder rolls off the processed area.

Figure 9. A processed metal surface with <2% reflectance shows a larger contact angle (left) than the unprocessed one with about 12% reflectance (right).
Figure 10 shows the spectral reflectance for various process conditions. A combination of proper pulse energy (i.e., 16 µJ), scanning speed (50–100 mm/s), and pitch (5 µm) creates surfaces with the lowest reflection, which is less than 2% over the whole spectral region. These optimal laser and process parameters for low reflectance are consistent with those for superhydrophobicity, which further confirms that both hydrophobicity and low reflectance require hierarchical structures with a relatively high aspect ratio of 1 (measured by ZYGO’s 3D optical profiler).

Reflectance is an important property of hydrophobic surfaces as it provides immense applications in several fields, such as solar energy. A low reflectance percentage means that a solar panel can absorb more light from the sun to convert into energy while maintaining superhydrophobic and self-cleaning properties.

We also performed preliminary experiments to evaluate the reliability and the durability of these laser-processed metals. The stainless steel metal surface had a high resistance to extreme temperature cycles. No contact angle changes were observed before or after the metal was exposed to extremely high (71 °C) and low temperatures (−40 °C) or to temperature shocks (from 20 °C to −40 °C). This indicates that the hierarchical structures on these metal surfaces will not likely be degraded or displaced by temperature-induced stress.

4. Summary and Conclusions

We developed an fs fiber laser surface-processing technique to achieve superhydrophobicity. Under optimal conditions (i.e., 200 kHz PRR, 16 µJ pulse energy, 100 mm/s scanning speed, 5 µm pitch), a contact angle of 171° and a rolling angle of less than 3° were achieved. Moreover, it took only five minutes to process a 1 × 1 inch sample, which was over 10 times faster than an fs solid state laser and involved much simpler preparation than coating methods. In a recent study, scientists achieved a contact angle of 167° using a nano-Bi$_2$O$_3$ coating, which was kept almost stable for 180 days after exposure to the natural environment [34]. However, coatings have the possibility of being subject to durability issues, such as weak bond quality, peeling, and erosion.

We have demonstrated that fs fiber lasers can create hierarchical structures on metals for the surface to exhibit multifunctional properties, such as superhydrophobicity, self-cleaning, and light-trapping. The homogeneity of the surface structure plays a critical role in superhydrophobicity, and there is a strong correlation between superhydrophobicity and reflectance, the latter providing a quick indicator of hydrophobic quality.

The present works lay a solid foundation to further optimize the process to achieve a higher speed as well as better quality, stability, and durability of superhydrophobic surfaces for any type and morphology of materials (e.g., metals, semiconductors, silicon, and glass). With these key advantages
and prospective advancements, these surfaces can upgrade the performance of biomedical devices, the efficiency of solar cells, the water-repellent abilities of infrared sensors, aircraft operation in harsh environments, and more critical applications in a wide array of industries.

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