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Topical Review

Bioinspired micro/nanostructured surfaces prepared by femtosecond laser direct writing for multi-functional applications

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Abstract

Femtosecond laser direct writing (FLDW) has been widely employed in controllable manufacturing of biomimetic micro/nanostructures due to its specific advantages including high precision, simplicity, and compatibility for diverse materials in comparison with other methods (e.g. ion etching, sol-gel process, chemical vapor deposition, template method, and self-assembly). These biomimetic micro/nanostructured surfaces are of significant interest for academic and industrial research due to their wide range of potential applications, including self-cleaning surfaces, oil-water separation, and fog collection. This review presents the inherent relationship between natural organisms, fabrication methods, micro/nanostructures and their potential applications. Thereafter, we throw a list of current fabrication strategies so as to highlight the advantages of FLDW in manufacturing bioinspired microstructured surfaces. Subsequently, we summarize a variety of typical bioinspired designs (e.g. lotus leaf, pitcher plant, rice leaf, butterfly wings, etc) for diverse multifunctional micro/nanostructures through extreme femtosecond laser processing technology. Based on the principle of interfacial chemistry and geometrical optics, we discuss the potential applications of these functional micro/nanostructures and assess the underlying challenges and opportunities in the extreme fabrication of bioinspired micro/nanostructures by FLDW. This review concludes with a follow up and an outlook of femtosecond laser processing in biomimetic domains.
Keywords: femtosecond laser direct writing, multiscale micro/nanostructures, extreme fabrication, bioinspired applications

1. Introduction

Nature often guides the practical applications of modern industrial extreme manufacturing [1–5]. As a result, bioinspired design from natural organisms, that exhibit extreme functional characteristics arising from their unique surface micro/nanostructures, have been implemented in radars [6], submarines [7], and airplanes [8–12], to obtain useful functionalities such as anti-wear [13], anti-corrosion [14], and self-cleaning [15–21]. One of the most attractive phenomena is the self-cleaning ability of lotus leaf, which as the poem by Dunyi Zhou says ‘She grows in mud, yet never contaminates with it. She floats on waving water, yet never dances with it’. The second paradigm is Namib desert beetles can survive in extremely dry and foggy deserts, which has implications for reducing fog in airports, collecting water for irrigation and collecting potable water in foggy, arid environments. These extreme biological characteristics possess unique surface topography and proper intrinsic wettability. The fluff and tiny-nanoscaled waxy particles endow the surface of the lotus leaf with superhydrophobic characteristics and self-cleaning capability. The combination of the superhydrophobic texture and superhydrophobic grooves on the surface of Namib desert beetles render their capability of sucking water vapor from moist air. As abundant water droplets accumulate in the superhydrophobic regions, they roll along the bow back and fall into the beetle’s mouth.

In order to obtain these functional micro/nanostructured surfaces, researchers have developed diverse micro/nanoprocessing methods, including reactive ion etching, sol-gel processing, chemical vapor deposition, electrochemical processing, template methods, self-assembly etc [22–30]. Unfortunately, these methods suffer from limitations. For instance, the processing steps are too complicated to control precisely; the processing platforms are limited to the specific materials; the processing environment is harsh; the fabrication process is always accompanied by secondary pollution and so is not environment-friendly. There is still an urgent need for new strategies of preparing biomimetic multifunctional surface micro/nanostructures efficiently, accurately, and easily. As a novel method of preparing micro/nanostructures, femtosecond laser direct writing (FLDW) technology has attracted great attention due to its ultrahigh processing accuracy, wide application for various materials, simplicity, and rapidity. Many reviews have reported the tremendous achievements of the FLDW technology towards advancing the field of micro/nanofabrication [31–33]. However, essential characteristics, such as the classification, formation mechanism, and design paradigm, of specific extreme micro/nanostructures have not been systematically summarized. A deep understanding of these essential characteristics is vitally important to the fabrication of biomimetic surface morphology through FLDW.

In this review, we present the correlation among natural organisms, fabrication methods, micro/nanostructures and potential applications. Then we compare the features of existing fabrication strategies and highlight the advantages of FLDW in preparing bioinspired microstructures. Subsequently, we present the bioinspired designs (e.g. lotus leaf, pitcher plant, rice leaf, butterfly wings, etc) and extreme femtosecond laser processing of diverse multifunctional micro/nanostructures (e.g. microhole, micropillar, hierarchical structure, nanoripple, self-growing structure). Based on the principle of interfacial chemistry and geometrical optics, we summarize the applications of various micro/nanostructures prepared by FLDW in the fields of structural color, self-cleaning, oil-water separation, fog harvesting, underwater bubble collection, droplet directional transport, and droplet/optical switch. Finally, we conclude with a summary of the challenges and opportunities associated with fabricating bioinspired micro/nanostructures by FLDW and an analysis of the future of femtosecond laser processing in biomimetic field.

2. Correlations among nature organisms, fabrication methods, micro/nanostructures and potential applications

Natural organisms have developed micro/nanostructures with tremendous attractive capabilities which induces abundant intriguing inspirations for human to utilize micro/nanofabrication methods to assimilate and/or emulate to develop diverse potential applications (figure 1). For instance, self-cleaning surfaces were inspired by the natural lotus leaf, which emerges from the mud unstained [34]. The compound-eye camera was inspired by the dragonfly’s compound eyes, which enable wide angle reconnaissance [35]. Structural coloration was inspired by butterfly wings, which produce brilliant iridescent colors when illuminated by the moonlight [36]. Dry tape was inspired by the gecko foot, which can grip even the slipperiest surfaces, giving rise to the lizards exceptional climbing abilities [37]. These biological functions have provided great impetus for scientists to develop similarly functional materials.

The hierarchical structure at the micro/nanoscale is recognized as the key element in determining the reproduction of these unique functions [38–43]. For example, covering multiscale micro/nanostructures in a thin layer of hydrophobic wax prevents pollutants from adhering to surfaces similar to the self-cleaning lotus leaf. Dust particles could be easily removed when liquid droplets roll over a lotus leaf, which is
laser power, scanning speed, and scanning period. Through the advanced micro/nanomanufacturing technology, we can replicate the unique biomimetic micro/nanostructures to harvest a variety of functions similar to those observed in natural organisms, including anti-icing [49], oil-water separation [50], energy conversion [51], bubble manipulation [52], structural color [53, 54], and anti-fogging [55, 56].

3. Interaction between femtosecond laser and solid substrate

As one of the most important means for humans to explore the microworld, micro/nanofabrication technology has extremely vital applications in fabricating microelectronics [83], microoptics [84], microfluidics [85], and other leading-edge fields [86–89]. Currently, widely adaptive technologies consist of planar lithography [90], electron beam etching [91], focused ion beam etching [92], chemical polymerization [93], and self-assembly [94] (figure 2). However, these micro/nanofabrication technologies have limited practical applications. For example, lithography is usually used in plane processing. The efficiency of non-plane processing will be significantly reduced (figure 2(a)). The rate and efficiency of reactive ion etching are relatively low. It is difficult to prepare multi-component films by electro chemical deposition, and the growth rate of crystal nuclei cannot be precisely controlled (figure 2(b)). Plasma treatments suffer from poor precision control, resulting in structures with rough surfaces (figure 2(c)). Electron beam etching and focused ion beam etching are expensive methods of micro/nanostructure fabrication. It should be noted that the intrinsic shortcomings of these traditional techniques limit their potential application in diverse fields.

In recent years, femtosecond laser direct micro/nanowriting technology has been widely adopted in the field of micro/nanomanufacturing (figure 2(d)) [95]. Due to its extremely short pulse width, a femtosecond laser can achieve extremely high peak power at the focal spot, even if the pulse energy is only in the order of microjoule or millijoule. Under strong light field conditions, the electric field intensity of the laser can distort the coulomb potential of most neutral atoms, causing a nonlinear interaction between light and matter, such as multi-photon absorption or tunneling ionization [96]. Compared with other micro/nanowriting technology that utilizes nanosecond pulsed light or continuous laser [97], FLDW offers several unique advantages: (1) high processing accuracy due to its relatively low thermal impact in the processing area; (2) high peak intensity, which makes FLDW processing suitable for almost any; (3) high processing resolution, especially for two photon polymerization because of the femtosecond nonlinear absorption effect; (4) the femtosecond laser has a long wavelength and excellent penetrability, making it suitable for true 3D fabrication. The mechanism of femtosecond laser induced controllable multiscale micro/nanostructures is related to three effects: laser ablation effect [98], laser-induced effect [99], and debris self-deposition [100].

![Figure 1. Correlations among nature organisms (bats [57], lotus leaf [58], water strider [59], rose petal [60], pitcher plant [61], butterfly wings [62] and desert beetle [63]), fabrication methods (lithography [64], reactive ion etching [65], electro-chemical deposition [66], plasma processing [67] and femtosecond laser direct writing [68]), micro/nanostructures [69–73] and potential applications (anti-icing [74], oil-water separation [75], energy conversion [76], bubble manipulation [77], structural color [78] and anti-fogging [79]).](image-url)
(1) Under the laser irradiation, the target material absorbs the laser energy and transforms into a liquid or gas. The molten liquid is expelled from the zone of action by recoil. The steam escapes directly from the focal point. During the process, some nanoparticles form around micropits, which result from the combined effects of laser shock compression and debris deposition [101]. Due to the short pulse width in the process of femtosecond laser induction, the vapor and plasma phases are rapidly generated with negligible conduction, and no liquid phase presents [102]. It is worth noting that the laser ablation effect contributes to the fabrication of various microscale structures (e.g. microhole, micropillar, and microgroove). At the same time, the nanoscale structures (e.g. nanoparticle) are also generated around the microscale structures due to the debris self-deposition effect [103].

(2) Another fabrication mechanism of surface structure is mainly derived from the laser-induced effect. The theories for the generation of periodic fringe structure induced by ultrashort pulse laser include self-organization [104], plasma excitation [105], and second harmonic generation [106]. Electromagnetic field energy of the incident plan wave does not distribute evenly on thin, rough surfaces (note that the surface thickness is much smaller than the wavelength of the incident light). The electromagnetic field energy distribution [107] determines the formation of periodic self-organizing fringe [107]. Periodic ripples are among the important induced fringe structures, and are widely employed in the manufacturing of special wettability surfaces [108] and metal coloring [109].

(3) Under the condition of liquid-assisted (source solution [110], ethanol [111], water [112] and so on) processing, femtosecond laser processing could produce unique structures different from those produced in an open-air environment. It should be noted that the fabrication process of liquid-assisted FLDW is more complex, consisting of five general phases, including laser-induced plasma effect of liquid, enhanced heat conduction, increased shock wave, intensified acoustic pressure, and explosive vaporization. The femtosecond laser may produce a superheated substance [113] around the target sample, which brings the surrounding liquid to a supercritical state [107]. The resulting pressure wave interacts with the liquid layer on the target surface, altering its morphology. The forming mechanism of micro/nanostructures fabricated by liquid-assisted FLDW is mainly related to the ultrahigh temperature of plasma ions excited at the liquid/solid interface, and the capillary wave during the cooling process. Additionally, the ablation process generates smaller bubbles around the target sample. The interaction between the liquid, bubble, and solid surface plays a critical role in the fabrication of specific micro/nanostructures.

In short, FLDW is efficient strategy for the fabrication of multi-functional micro/nanostructures. FLDW involves various interactions between the laser pulse and materials (e.g. laser ablation effect, laser-induced effect, and debris self-deposition), which have broad applications in diverse fields, such as surface modification and fabrication of intelligent micro/nano devices.
4. Typical micro/nanostructures by FLDW

4.1. Microhole arrayed structure

The microhole arrayed structure is a typical micro/nanostructure fabricated by femtosecond laser drilling metal or polymer films (figure 3). The inner walls of the microholes drilled by femtosecond laser are smoother and cleaner than those drilled by picosecond or nanosecond laser. For example, Wu et al. presented a type of regular microhole arrayed aluminum foil ablated by femtosecond laser for efficient oil/water separation (figure 3(a)) [117]. Wu et al. precisely controlled the diameter of the microholes (2.4 µm–32 µm) by adjusting the laser power and pulse number (figure 3(b)). Chen et al. designed and fabricated a microhole arrayed Janus PDMS surface based on femtosecond laser drilling to achieve the unidirectional self-transport of underwater bubbles. The microhole diameter could also be precisely controlled by adjusting the laser pulse numbers [115]. Zhang et al. proposed a simple, functional device for oil/water separation utilizing an aluminum film (oil barrel), covered in an array of tapered microholes induced by femtosecond laser ablation [119]. Recently, Yan et al. fabricated a Janus aluminum film with tapered microholes using femtosecond laser ablation and selective laser removal of fluorinated areas [118] (figure 3(c)). Yan et al. reported no fluorine signal on the bottom surface of the film, which indicates that selective femtosecond laser scanning completely removed the fluorination material on the bottom surface (figure 3(d)).

4.2. Micropillar arrayed structure

The micropillar arrayed structure is fabricated by orthogonally decussate line laser scanning on metal or polymeric surfaces. The surface micropillar arrays can be utilized to construct superwetting interfacial materials (figure 4). For instance, taking hints from the underwater superaerophobicity of fish scales, Yong et al. designed and fabricated multiscale structures on silicon by femtosecond laser [120]. It can be seen from the SEM images that the period and the size of the micromountains was 10 µm and 7–8 µm, respectively. Additionally, there were abundant nanoparticles on each micromountain (figure 4(a)). Chen et al. manufactured a
hydrophobic micropillar arrayed zinc oxide film (ZOF) using femtosecond laser ablation to realize the in-situ reversible tuning of diverse liquids between the sliding and pinning state under ultra-low voltage [121]. It is worth noting that the micropillar arrayed ZOF was covered with paraffin under the effect of capillary force (figure 4(b)). This is the key to achieving dynamic control of droplet movement on the surface, which is confirmed by the sectional and top view of ZOF (figure 4(c)). Moreover, Chen et al. reported a simple strategy for fabricating superhydrophobic PDMS microlens arrays by wet etching and femtosecond laser direct writing. The fabricated samples exhibited outstanding imaging features and self-cleaning functions (figure 4(c)) [122]. Their research team recently utilized femtosecond laser to prepare hierarchical micropillar arrays (diameter ~ 20 µm, height ~ 45 µm, space ~ 40 µm) on shape-memory polymers, which imparted the surface with superhydrophobicity. The micropillar array could realize the reversible tuning between the tilted and upright state under the heating condition (figure 4(d)).

4.3. Micro/nano hierarchial structure

Micro/nano hierarchical structure is a type of composite structure that contains both microscale and nanoscale structural components, which plays a key role in the preparation of extreme wetting surfaces (e.g. superhydrophobicity, superhydrophilicity). In general, a single microstructure or nanostructure may exhibit hydrophobic characteristics, but its rolling angle is relatively high on account of the high adhesion. Only the surfaces with composite micro/nanostructures (e.g. rice leaf and lotus leaf) can impart a lower adhesion force between droplets and the solid surface, achieving a lower rolling angle (<10°) and a higher contact angle of droplets (>150°). Lu et al. reported a simple and effective method of fabricating hierarchical microgrooved structures on PDMS films by using an energy-tuning laser scanning strategy (figure 5(a)). Firstly, the macrogrooves with anisotropic feature were achieved by laser ablation with large power. The superhydrophobic micro/nanostructures were fabricated under a low laser power.
The as-prepared surface had an obvious anisotropic sliding ability and the difference of sliding angle along the perpendicular and parallel direction was about 6°, which was similar to the real rice leaf [124]. Chen et al reported a versatile, bioinspired superhydrophobic surface with tridirectional anisotropic sliding ability (figure 5(b)). They used selective laser processing to constructed the microgroove arrayed PDMS surface, which showed bidirectional anisotropic properties. Additionally, the bidirectional anisotropic ability could be tuned by the height and period of the microgrooves (figures 5(c) and (d) [125].

4.4. Self-growing structure

Though bioinspired architectures (e.g. micropillars, microholes, and microcones) have been widely explored, most of these structures are based the material-reducing process during laser ablation. These structures have no shape transformation in a bulk material in response to external stimuli. Recently, Zhang et al introduced a ’self-growth’ strategy to achieve a localized reconfigurable microstructure transformation on a pre-stretched shape-memory polymeric material through precisely controlling the femtosecond laser ablation (figure 6). These results suggest that it is possible to prepare micropillar structures in one step through the interaction of femtosecond laser with heat-shrinkable polymers (figure 6(a)). Additionally, the as-prepared upright micropillars bend when the laser focus scans another semicircular path (figure 6(b)), which is defined as the asymmetric laser scanning strategy. It is worth noting that the interactions between the laser pulse and the polystyrene materials (e.g. ablation and heating) play an important role in the formation of bent and upright micropillars. On the basis of the mechanical model and analysis (figure 6(c)), the growth mechanism of micropillars consists of four periods as the repeat circles increase. Additionally, various ordered patterns could be achieved by utilizing the bent micropillar as a unit. These intelligent architectures will
find wide applications in industries that rely on information encryption/decryption and particle trapping, such as microstructure printing anti-counterfeiting, and ultrasensitive detection [126].

4.5. Induced nanoripple arrayed structure

The nanoripple arrayed structure is a type of special nanostructure composed of nanometer-wide stripes arranged in a periodic, continuous manner. Nanoripple arrayed structures frequently appear in nature. For example, butterfly wings often contain striped structures arranged periodically. The direct interaction between these structures and incident light endows the butterfly its brilliant colors. It is worth noting that FLDW can induce periodic fringes on the surface of various materials (e.g., metal, semiconductors, and insulators). Studies have revealed that the direction of the periodic stripe is perpendicular to that of the laser polarization. The theories for the generation of periodic fringe structures induced by an ultrashort pulse laser include self-organization, plasma excitation, second harmonic generation, etc. In 2009, Sakabe et al. divided femtosecond laser induced stripe structure formation into three steps [128]: (1) the femtosecond laser induces plasma waves on the metal surface; (2) the first few pulses of the femtosecond laser forms periodic streaks on the surface and the subsequent process involves a single pulse; (3) the electric field is enhanced at the fringe structure, formed by the subsequent pulse, and then melts the metal surface deepening the periodic structure. As mentioned above, the induced nanoripple arrayed structures are used in the fabrication of special wettability materials and structural color. For instance, Li et al. used a femtosecond laser micro/nanoprocessing system to achieve structural color applications on stainless steel (figure 7(a)) [127]. The modified surface structure morphology on the stainless steel was detected by a scanning electron microscope (figure 7(b)), which revealed that the ripples,
Figure 7. Induced nanoripple arrayed structure. (a) Experimental apparatus for stainless steels fabrication and the schematic of color detecting system [127]. (b) Partial SEM pictures for the laser-induced periodic microstructures by various laser wavelength. (a), (b) [128] (2015) With permission from Springer.

4.6. Other micro/nanostructures induced by liquid-assisted FLDW

Recently, many research groups have focused on liquid-assisted FLDW, which can fabricate distinct micro/nanostructures compared to those created through FLDW in air [129–139]. Li et al conducted research on the preparation of various controllable micro/nanostructures by liquid-assisted femtosecond laser ablation [114, 129, 130] (figure 8). They employed different liquids (e.g. ethanol, sucrose, and water) to obtain microcones and micromolar silicon arrays (figures 8(a) and (b)) with tunable wettability. They studied the relationship between the structural parameters (figures 8(c) and (d)), surface roughness (figure 8(e)), and pulse energy to precisely control the microstructure. The formation mechanism of these micro/nanostructures by liquid-assisted FLDW related to the ultrahigh temperature of plasma ions excited at the liquid/solid interface and the capillary wave during the cooling process. It should be noticed that there would generate more and smaller bubbles in water-assisted ablation than that in sucrose solution-assisted ablation. This is because of differences in the viscosity, density, and boiling points of these two liquids, which have enormous effects on the microstructure morphology of silicon.

5. Multi-functional applications of micro/nanostructures

As the fast development of bionics and femtosecond laser extreme processing technology, a variety of powerful interface materials and devices that combine with these extreme micro/nanostructures have been designed and manufactured. These interfacial materials and devices can be adapted to meet diverse functional applications, including oil-water separation, fog harvesting, anti-icing, structural color, droplet and bubble manipulation, and anti-reflection.

5.1. Oil-water separation

Oil-water separation is one of the most crucial technological processes in the oil industry. Due to frequent oil spill accidents, the problems of resource waste and environmental pollution are becoming more and more serious (figure 9). Oil spill
accidents severely contaminate and endanger marine ecosystems. In recent years, oil spills have resulted in the deaths of a large number of natural organisms [140]. Researchers have proposed several solutions to solve this issue, including air-float separation [141], gravity separation [142], and centrifugal separation [143]. Oil-water separation materials prepared by femtosecond laser extreme manufacturing methods also show promising results. Wu et al reported a Janus oil barrel based on the tapered microhole arrayed aluminum film to achieve spontaneous collection of spilled oil with an ultrahigh flux (45 000 Lm$^{-2}$ h$^{-1}$) for further oil/water separation [119]. Firstly, femtosecond laser drilling was utilized to prepare the double-faced superhydrophilic aluminum membrane and the diameters of the microholes were precisely regulated by adjusting the laser power and pulse numbers. After the fluorination modification and the selective laser removal of the modification area, the Janus barrel was harvested. Hu et al also reported a novel aluminum film covered by large-area regular micropores [117], which performed continuous high-speed oil-water separation and oil collection. Yin et al proposed a versatile strategy to prepare stainless steel mesh with periodic nanoripples induced by femtosecond laser, which possess superhydrophilic and underwater superoleophobic properties. The interfacial materials showed robust stability after abrasion tests and longevity tests [144].

5.2. Fog harvesting
Fog harvesting based on bioinspired micro/nanostructured surfaces with specific wetting ability has attracted attention as possible solution to the water shortage plaguing modern society (figure 10). One of the most important bioinspired phenomena is the hump-like surface microstructure inspired by the Namib desert beetle’s back, which possess excellent fog collection capabilities. Ren et al designed and fabricated a Janus (hydrophobic/hydrophilic) aluminum film covered by gradient conical micropore arrays for efficient fog collection [116]. It is worth noting that the collection on the Janus film is nearly twice as efficient compared with the original superhydrophilic film, which shows a great potential application in constructing a water collection device to alleviate the freshwater crisis. Inspired by the beetle’s elytra, Kostal et al utilized a simple three-step preparation strategy to increase the collection efficiency of glasses. It was demonstrated that high-contrast wetting surfaces collected the most fog and increased the fog-collection efficiency by ~ 60% compared to the pristine
Pyres glass [145]. Yin et al. reported a novel high-efficiency strategy to prepare a Janus microstructured membrane covered with nanoparticles on copper foam by femtosecond laser microfabrication. The fabricated Janus membrane was able to collect water in foggy conditions with a maximum collecting efficiency of \( \sim 3.7 \) g \( \text{(cm h)}^{-1} \) [146]. Recently, they also proposed a hybrid hydrophilic-superhydrophobic surface on the copper mesh which contained micro/nanopatterns induced by femtosecond laser ablation [147]. The Janus film based on copper mesh could significantly enhance the fog collection efficiency, which could be controlled by adjusting the inclination angle, mesh number, and surface microstructure. In addition, it was noted that the as-prepared surface exhibited outstanding anti-corrosion ability after immersing it in NaOH, HCl, and NaCl solutions, which may promote its application in water collection.

### 5.3. Anti-icing

Icing is a common natural phenomenon. Under certain conditions, the attachment and accumulation of snow and ice poses significant economic losses and potential safety hazards. Thick ice on power lines threatens the safe operation of power, railway, and communication networks [148]. Current ice removal methods are summarized as mechanical method [149] and melting strategy [150]. But these methods are utilizing complex structural design and require large amounts of additional energy consumption. Superhydrophobic surfaces have received extensive attention, showing great potential in self-cleaning. The superhydrophobic materials have demonstrated outstanding ice resistance (figure 11). Zhong et al. studied the underlying mechanism in fabricating surface micro/nanostructures by ultrafast laser [151]. Furthermore, the influences of surface micro/nanostructures on the adhesion, anisotropy, stability and anti-icing performance of superhydrophobic surfaces were systematically studied. There are four kinds of typical hydrophilic nanostructures, whose morphology were mainly decided by the laser scanning parameters, including the scanning interval and pattern. When the hydrophilic metal surfaces were placed in air, they spontaneously turned into highly hydrophobic surfaces due to the adsorption of organic matters onto the metal oxide. It can greatly delay the icing process of surface water droplets under frost-free condition. Under temperatures between \(-10 \sim 6 \) °C, water droplets on superhydrophobic surfaces maintain their liquid state for 12 h without icing.
5.4. Structural color

The structural color induced by periodic textures on solid substrates has received great attention in both academic and industrial fields. In most situations, structural color textures are considered a kind of grating structure originating from the diffraction of light (figure 12), which is a simple and vital strategy to change the optical performance of metal surfaces. The surface texturing by femtosecond laser is a versatile and simple way to generate structural colors. For instance, Li and Hu \textit{et al.} proposed a strategy to display various colors induced by surface microstructures through simultaneously adjusting the incident light angle and ripple orientation [127]. In addition, different patterns composed of ripples could be precisely designed and controlled by adjusting the incident white light angle and rotating the sample angle. Recently, Wu \textit{et al.} reported a microstructured metal surface utilizing a focused laser interference lithography fabrication strategy, which exhibited various structural colors. The water droplet showed an anisotropic wetting ability on the surface. It is worth noting that the fabrication strategy of generating structural color is suitable for multiple materials, such as copper, titanium, iron, etc. Li \textit{et al.} proposed controllable parameters (e.g. laser wavelength, spatial period and incline angle) to generate different colors, which could apply to a large range of applications in the art design and laser color marking [152].

5.5. Droplet and bubble manipulation

Droplet and underwater bubble manipulation are vital for both industrial and academic researches due to their practical applications in water treatment, sensors, and microreaction technology. There are several methods (e.g. electric, magnetic, light and thermal actuation) of manipulating the droplet/bubble motion. For instance, electro wetting actuates...
the droplet motion through the variation of contact angles [153]. The magnetic actuation requires mixing magnetic nanoparticles into the droplets so the droplets respond to external variations in magnetic fields and achieve directional movement [154]. The local temperature of the sample can be significantly altered by thermal stimulus to form a surface tension gradient to actuate the droplet [155]. Moreover, inspired by natural organisms, many functional surfaces with tailored geography and biomimetic microstructures have been artificially realized (figure 13). For instance, Chen et al prepared a Fe$_3$O$_4$ doped slippery PDMS surface with light response by femtosecond laser crossed ablation [156]. The surface achieved the directional transport of underwater bubbles by loading/discharging a near-infrared light stimulus. The driving mechanism was related to the wettability gradient force due to the high temperature difference. Li et al designed an intelligent droplet motion device composed of paraffin wax, micropillar-arrayed zinc oxide film (ZOF) and a flexible silver nanowire heater [121]. The hydrophobic ZOF was fabricated by femtosecond laser microfabrication to realize the in-situ reversible tuning of droplet sliding movement by mechanical stretch, which was related to the variation of contact angle hysteresis [157]. Jiao prepared a large-area oil infused slippery surface for bubble self-transport and highly efficient gas capture, which was also controlled by the competing forces: resistance (drag force and contact angle hysteresis) and buoyancy [158]. It is worth nothing that differently shaped slippery tracks were prepared to achieve the precise manipulation of underwater bubbles, which may have potential applications in the fields of bubble merging and detachment. Recently, Yong et al also reported a porous network of microstructures on different polymer materials [159]. Through the surface modification and oil-infused process, the porous slippery surface showed an outstanding lyophobic ability, which greatly inhibited C6 glioma cells.

5.6. Anti-reflection

Functional surfaces and interfaces that reflect minimum electromagnetic waves over a wide spectrum range have vital

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**Figure 11.** Anti-icing [151]. (a) Ice formation procedure on different Cu sample surfaces. (b) Shape of the droplet on different sampled surfaces before and after freezing. (c) Water contact angle of the superhydrophobic samples fabricated by femtosecond laser versus temperature. (d) Ice formation delay time versus samples under different temperatures. (a)–(d) Reproduced with permission from [151].
significance for military aircraft equipment. Nevertheless, there are challenges to achieving effective anti-reflection on solid substrates due to the optical impedance mismatch. Most anti-reflection candidate coatings are unable to bridge gaps in the refractive index, which result in the effectiveness of traditional destructive interference coatings and gradient refractive index membranes. Recently, the developed strategies for anti-reflection coatings are limited to non-metal micro/nanostructured materials (figure 14). Zhong et al developed a simple strategy for fabricating hybrid anti-reflection micro/nanostructures on different metal surfaces by a femtosecond laser direct writing method [160], which was modified by controlling the laser pulse injection and flexible modifications. Guo et al fabricated a versatile large-area grating structure superimposed by finer nanostructures on a silicon surface, which exhibited an anti-reflection effect in the wavelength range from 250 to 2500 nm [161]. These periodic structures induced by femtosecond laser can restrain both the total hemispherical and specular polarized reflectance, which has many advantages, including no environmental contamination and the ability to precisely control the size of the microstructure. Vorobyev et al designed the microgroove arrays on silicon substrates covered with nanostructures, which exhibited a significant reflectance reduction [162]. Further investigation suggests that the anti-reflection range can be expanded to the mid-infrared wavelength. For instance, Cheng et al designed and fabricated a series of silicon surfaces with textured anti-reflection membranes by femtosecond laser fabrication, which demonstrated a 30% increase of the transmittance response [163].

6. Outlook and conclusion

The fabrication of bioinspired multiscale structures with diverse functions by FLDW has obtained great achievements due to its superior processing characteristics. However, there are still great challenges to face in the FLDW: (1) the interaction mechanism between femtosecond laser and various metallic and non-metallic materials has not been thoroughly studied, and the interaction between some new materials (e.g. shape memory polymer and alloy) and femtosecond laser to produce new structures requires further investigation; (2) femtosecond laser fabrication has some limitations, such as high processing
cost and long processing time, especially in the preparation of large area surfaces for practical applications. Strategies can be provided such as parallel processing of femtosecond laser by programming and high-power laser and high-speed scanning processing; (3) over current research, it is difficult for a single processing method to meet the requirement of achieving the desirable structure and performance, so it is necessary to develop a variety of methods to co-produce biomimetic micro/nanostructures. How to integrate femtosecond laser fabrication technology with other processing methods for achieving the highest efficiency and lowest cost is still an important research question; (4) how to choose the correct structural surface to maximize the application efficiency of the material, such as straight hole arrays or cone hole arrays for oil-water separation is worth studying. Despite the great advances in the technological content, the application of nature-inspired functional surfaces fabricated by FLDW in industrial engineering is still difficult to realize. One of
the key reasons is that the unique ability of these functional materials works well in the laboratory conditions, but could fail in massive industrial production. Therefore, addressing these challenges will advance our fundamental understanding of the mechanisms underlying biological functional surfaces and inform effective methods of producing bioinspired material designs and fabrications for industrial applications.

In this review, we highlighted the utilization of FLDW to achieve the extreme manufacturing of various bioinspired micro/nanostructures, such as microhole, micropillar, hierarchical structure, self-growth structure, and nanoripple. We also summarized crucial applications for laser-ablated micro/nanostructured surfaces in the fields of oil-water separation, anti-icing, fog harvesting, and structural color. It is noteworthy that these nature-inspired functional surfaces have penetrated nearly every aspect of traditional mechanical systems and daily life. However, there is a great step to realize the practical usability of these functional surfaces in massive industrial production by the laser ablated strategy. Through the tireless efforts of broadening the research field of femtosecond laser and deepening the research direction, we believe the femtosecond laser biomimetic structure will be widely-applicable for practical usability in the near future.

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Author contributions

D W and Y J conceived this review. Y Z and Y J wrote the manuscript and they contributed equally. Y Z, Y J, C L, C C, J L, Y L, D W and J C participated the modification of the manuscript. The authors declare that there is no conflict of interest regarding the publication of this paper.
References

[1] Sanchez C, Arribart H and Guille M M G 2005 Biomimetic design and bioinspiration as tools for the design of innovative materials and systems Nat. Mater. 4 277–88


[33] Yong J L, Yang Q, Guo C L, Chen F and Hou X 2019 A review of femtosecond laser-structured superhydrophobic or underwater superoleophobic porous surfaces/materials for efficient oil/water separation RSC Adv. 9 12470–95

[34] Marmar A 2004 The lotus effect: superhydrophobicity and metastability Langmuir 20 3517–9


[57] Popa-Lisseau A G and Voigt C C 2009 Bats on the move J. Mammal 90 1283–9


[60] Bhushan B and Nosonovsky M 2010 The rose petal effect and the modes of superhydrophobicity Philos. Trans. R. Soc. A 368 4713–28


[65] Li X H, Abe T and Esashi M 2001 Deep reactive ion etching of Pyrex glass using SF6 plasma Sensors Actuators A 87 139–45


[68] Zhang Y L, Chen Q D, Xia H and Sun H B 2010 Designable 3D nanofabrication by femtosecond laser direct writing Nano Today 5 435–48


[99] Paiuplas D, Mizeikis V, Purlys V, Cerkauskaite A and Juodkazis S 2015 Volumetric integration of photorefractive micromodifications in lithium niobate with femtosecond laser pulses Proc. SPIE 9374 93740B
[121] Chen C et al 2019 In situ reversible control between sliding and pinning for diverse liquids under ultra-low voltage ACS Nano 13 5742–52
surfaces by femtosecond laser Adv. Mater. Interfaces 5 1701245


[155] Xu X P and Qian T Z 2012 Thermal singularity and droplet motion in one-component fluids on solid substrates with thermal gradients Phys. Rev. E 85 061603


