Femtosecond-laser-induced backward transfer of fluorinated ethylene propylene for fabrication of “lotus effect” surfaces

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"Lotus effect" glass surfaces with fluorinated ethylene propylene were successfully fabricated by using a femtosecond laser-induced backward transfer (LIBT) method. By space-selectively modifying both the surface morphology and surface chemistry in a single step, LIBT provides a convenient and flexible route to fabricate superhydrophobic surfaces with ultralow adhesion. A systematic mechanism responsible for the anisotropic wetting behaviors and adhesion modulation was proposed with a combination of the Cassie and Wenzel models. X-ray photoelectron spectroscopy revealed that oxidation and defluorination were induced by laser radiation. LIBT is proved to be a promising method for programmable manipulations of functional surfaces with diverse wettability.

Keywords: superhydrophobic surface; laser-induced backward transfer; fluorinated ethylene propylene; glass.
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1. Introduction

Superhydrophobicity, which indicates a water contact angle (CA) of more than 150°, is a common property in nature[1]. The Lotus effect, as a special type of superhydrophobicity, attracted enormous attention due to its low adhesion, which has been successfully used for self-cleaning, anti-corrosion, anti-sepsis, non-fouling, chemical shielding, oil-water separation, etc.[2–9].

Superhydrophobicity is believed to be a physiochemical phenomenon that depends on two key aspects: surface energy and surface microstructures[10,11]. For fabricating “lotus effect” surfaces, versatile methods have been applied. For example, laser direct writing was used to produce micro-protrusion array structures on surfaces of alloy[12]; spray coating technology was used to assemble silicone-based paint into films on solid substrates[13]; the lithography method was used to print a petal-like structure on preprocessed wood, which was firstly placed into the precursor PVB/SiO2 solutions[14]. But, laser direct writing and spray coating can only modify surface microstructures and surface chemistry, respectively. For the lithography method, multi-steps including stamp preparation, solvothermal processing, and nanoimprint processing were even applied, which was somewhat complex and cost expensive. Despite the already used techniques, there is still a great demand for a more convenient and flexible route to fabricate “lotus effect” surfaces. In addition, further reduction of surface adhesion to the extent that the sliding angle of a water droplet approaches zero is still a great challenge ahead.

Laser-induced backward transfer (LIBT) is an emerging technology that enables space selective modification of both the surface microstructures and surface chemistry in a single step. LIBT was first reported, to the best of our knowledge, by Bohandy et al.[15], in which Cu was transferred from metal plates to a silicon plate. Nowadays, LIBT is commonly used for microprinting of diffractive optical structures and computer-generated holograms, writing active and passive mesoscopic circuit elements, producing nanoparticles and 3D microstructures, as well as for biomolecule printing applications, etc.[16,17]. However, LIBT has rarely been used for the fabrication of “lotus effect” surfaces. In order to obtain superhydrophobic surfaces by the LIBT process, receiving substrates are only required to be transmissive for lasers. Ordinary commercial glass can easily meet the demand. In contrast, donor substrates should be
Fluorinated ethylene propylene (FEP) is a typical fluoride with low surface energy and has been previously used for fabricating superhydrophobic surfaces by utilizing hot embossing, UV radiation, etc. [18,19]. However, these methods can only fabricate superhydrophobicity on materials with low surface energy. To the best of our knowledge, FEP has scarcely been designed for substrates. Therefore, FEP was selected as the donor substrate.

In this study, LIBT was successfully used to fabricate “lotus effect” surfaces by enhancing roughness and coating a thin layer of FEP on glass surfaces. With CAs improved to more than 150°, surface adhesion was further reduced down to the minimum that a 5 μL water droplet could not stick onto the glass surface. The dependence of anisotropic wetting behaviors and adhesion modulation on laser power and scanning interval was systematically investigated, and a combination of the Wenzel and Cassie models was proposed to evaluate the wetting performances. Combined with high-power lasers and high-speed scanning systems, LIBT is expected to be an advanced manufacturing method for large-scale fabrication of superhydrophobic surfaces with high-processing resolution.

2. Experiment

FEP films with a thickness of 200 μm were used as the donor substrates. The receiving substrates were soda lime microscope slides with dimensions of 76 mm × 25 mm × 1 mm. A fs laser (Pharos-SP-10W, Light Conversion) with wavelength of 1030 nm, pulse width of 182 fs, and pulse frequency of 100 kHz was used for LIBT. As shown in Fig. 1(a), the FEP film was tightly bonded to the glass surfaces, and, after transmitting through the glass (receiver), the fs laser was focused onto the interface between the glass and FEP films (donor) by a 10x objective lens (NA = 0.3). FEP films were then transferred to the glass substrate by implementing a parallel line raster pattern process. The laser scanning speed was set at 20 mm/s, and the scanning interval was varied from 10 to 70 μm. Using LIBT, the morphology and chemical components of the glass surface were modified at the same time.

The morphology of the glass surface was revealed via an optical microscope (VHX-7100, Keyence) and a scanning electron microscope (SU8100, Hitachi). The CAs were measured by specific equipment (SL200B, Kino), and a 5 μL water droplet was captured by a commercial CCD (EM-MV-200C, Microvision). In addition, chemical components of the glass surface were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250xi).

3. Results and Discussion

The CAs before and after the LIBT process are compared in Figs. 1(b) and 1(c). Before the LIBT process, the glass surface was hydrophilic with a CA of 17.1°. However, when proper laser parameters were selected, the glass surface was roughened and, at the same time, coated by a thin FEP layer. As a result, the CA increased to 161.9°. More importantly, a 5 μL water droplet could easily leave the surface with the rising needle even pressing it [Fig. 1(d)], indicating extreme water repellence. Therefore, the LIBT process has transformed a hydrophilic adhesive glass surface into a superhydrophobic non-adhesive glass surface, which is a typical “lotus effect.” The hydrophobicity remained stable after 3 months.

The dependence of water CAs on laser power at the scanning intervals of 10 μm, 30 μm, 50 μm, and 70 μm is shown in Figs. 2(a)–2(d). To test the anisotropic wettability, the static water CAs in two vertical directions, which were defined as the parallel direction and perpendicular direction with respect to the scanning line, were measured. At a scanning interval of 10 μm, the CAs of more than 150° could be achieved within laser power of 0.5–1.5 W, and there was little difference of CAs in the two vertical directions [Fig. 2(a)]. As mentioned in Fig. 1(c), when CAs reach more than 150°, the surface adhesion becomes so low that sticking of droplets on superhydrophobic glass could not be achieved. Therefore, in addition to CAs measured in two vertical directions in Fig. 2, a third label of a green cross is introduced to indicate ultralow adhesion. When the scanning interval was increased to 30 μm, CAs of more than 150° could only be achieved within a much smaller range of laser power (0.7–0.9 W). Besides, an apparent difference of CAs measured in the two vertical directions existed. With the scanning interval further increasing to 50 μm and 70 μm, the proper range of laser power to achieve superhydrophobicity was further reduced, and the difference value of CAs between two vertical directions was...
further enhanced. It can be seen that when the scanning interval was 70 μm, CAs of more than 150° could only be obtained at the optimum laser power of 0.8 W. Except for the optimal laser power, there was a large degree of difference of CAs measured along the two vertical directions within laser power of 0.5–3 W. The results above demonstrate that for each scanning interval, a laser-power window for superhydrophobicity exists. As long as the appropriate laser parameters are selected, glass surfaces with the "lotus effect" can be simply obtained by the LIBT process.

The effect of surface morphology on wettability is illustrated in Fig. 3. When the scanning interval was 10 μm, all scanning lines overlapped with each other so that the whole glass surface was covered by a thin layer of FEP. However, when the scanning interval was further increased to 30 μm, 50 μm, and 70 μm, no overlapping of scanning lines could be seen, and anisotropic wettability became apparent. At a laser power of 0.5 W, the FEP layer transferred to the glass surface stayed relatively neat. When the laser power was 0.8 W, fluctuations in the density and altitude generated by impact stress began to appear around the scanning lines [Figs. 3(i)–3(l)] and then became stronger with increasing laser power [Figs. 3(a)–3(h)]. From the whole evolution of wetting ability, we can find that the scanning interval is the most important factor accounting for anisotropic wettability, which will be systematically discussed in the following section.

Component analysis of the surfaces was performed using XPS. The initial glass and pristine FEP were also XPS-analyzed for comparison [Fig. 4(a)]. The peaks of F 1s and C 1s on the treated glass surfaces confirmed the presence of carbon and fluorine, which was evidence that FEP was successfully transferred. Another two obvious peaks of Na 1s and O 1s were the intrinsic signals of soda lime microscope slides. Considering the nanoscale penetration depth of XPS, we can assume that the thickness of the FEP layer was approximately 10 nm. To further confirm that the chemical groups transferred onto the glass surface, curve fittings of C 1s peak for FEP, and for glass surfaces treated at varied laser powers are compared in Figs. 4(b)–4(d). In addition, each deconvolution band of C 1s peak was assigned to its corresponding chemical groups, and their relevant percentage was calculated in Table 1. In pristine FEP, $(-C*F_2-CF_2)...$ at 292 eV was the dominant chemical group. Due to the photooxidation effect, a new chemical group of $CF-O-C*F_2$ began to appear at the laser power of 0.5 W. With the laser power further increased to 3 W, $CF-O-C*F_2$ became the prevalent chemical
Moreover, the pulse’s energy deposited over the time scale of fs ensured a minimal amount of heating and melting, with no harmful substances spraung into the air.

During the LIBT process, laser radiation, on the one hand, provides the driving force for FEP transfer and, on the other hand, causes oxidation and defluorination. FEP transferred onto the glass surface enhances wettability owing to its low surface energy \([23]\). However, both oxidation and defluorination cause higher surface energy, which degrades water repellency \([23]\). The two factors compete with each other, so an optimum laser-power window exists for superhydrophobicity, which has been clearly illustrated in Fig. 2.

The influence of scanning interval is discussed as follows. As mentioned in Fig. 1(b), an initial glass surface exhibits hydrophilicity and high adhesion, which is a typical Wenzel state. When the entire glass surface is coated with a thin layer of FEP using LIBT [as shown in Fig. 3(i)], the hierarchic structure of FEP film traps air under the water, leading to the Cassie–Baxter wetting behavior. On the basis of the above mentioned, we propose a mechanism responsible for the wetting states at different intervals in Fig. 5.

When the scanning interval was so small that the transferred FEP films overlapped with each other, it led to a typical Cassie–Baxter wetting behavior [Fig. 5(a)]. In this state, superhydrophobicity with ultralow adhesion can be readily obtained at a large range of laser powers. However, with an increase of interval, the uncovered zone by FEP film increases, and Wenzel states gradually dominate the wetting performance, which results in lower CAs and larger adhesion [Fig. 5(c)]. Anisotropic wettabiliy can also be explained by this model, as depicted in Figs. 5(d)–5(i). Energy barriers (EBs) are an influential factor for water diffusion \([28,29]\). In this experiment, EBs of the FEP coated zone were larger than that of the uncovered area. In the case of Fig. 5(a), the EBs are almost the same in two vertical directions [Figs. 5(d)–5(f)]. Therefore, a water droplet on the glass surface exhibited a nearly perfect sphere with negligible anisotropy. In the case of Fig. 5(c), water only needs to overcome low-EBs in the direction parallel to scanning lines [Fig. 5(h)]. In contrast, both low and high-EBs have to be conquered in

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**Table 1. Curve Fittings of C 1s Peak (in atomic fraction, %) for FEP and Glass Surface Treated by LIBT Process.**

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FEP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>292</td>
<td>((-\text{C}^*\text{F}_2-\text{CF}_2-)_n)</td>
<td>81.6</td>
</tr>
<tr>
<td>290.5</td>
<td>((-\text{C}^*\text{F}_2-\text{CH}_2-)_n)</td>
<td>10.63</td>
</tr>
<tr>
<td>289.9</td>
<td>(\text{C}^*\text{F}_3)</td>
<td>8.21</td>
</tr>
<tr>
<td>292</td>
<td>((-\text{C}^*\text{F}_2-\text{CF}_2-)_n)</td>
<td>42.46</td>
</tr>
<tr>
<td>0.5 W</td>
<td>(\text{CF}-\text{O}-\text{C}^*\text{F}_2)</td>
<td>33.55</td>
</tr>
<tr>
<td>293.7</td>
<td>(\text{C}^*\text{F}_3)</td>
<td>9.01</td>
</tr>
<tr>
<td>284.8</td>
<td>(\text{C}^*\text{C})</td>
<td>4.43</td>
</tr>
<tr>
<td>290</td>
<td>(\text{C}^*\text{F})</td>
<td>4.3</td>
</tr>
<tr>
<td>286.77</td>
<td>((-\text{CF}_2-\text{C}^*\text{H}_2-)_n)</td>
<td>3.41</td>
</tr>
<tr>
<td>288.8</td>
<td>(\text{C}=\text{O})</td>
<td>2.85</td>
</tr>
<tr>
<td>3 W</td>
<td>(\text{CF}-\text{O}-\text{C}^*\text{F}_2)</td>
<td>76.53</td>
</tr>
<tr>
<td>293.2</td>
<td>(\text{C}^*\text{F}_3)</td>
<td>8.59</td>
</tr>
<tr>
<td>284.8</td>
<td>(\text{C}^*\text{C})</td>
<td>6.08</td>
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<tr>
<td>286.77</td>
<td>((-\text{CF}_2-\text{C}^*\text{H}_2-)_n)</td>
<td>3.09</td>
</tr>
<tr>
<td>289.7</td>
<td>(-\text{C}^*\text{F}-\text{CF}_2-\text{CF}_3)</td>
<td>2.8</td>
</tr>
<tr>
<td>288.8</td>
<td>(\text{C}=\text{O})</td>
<td>2.91</td>
</tr>
</tbody>
</table>
the direction perpendicular to scanning lines [Fig. 5(i)]. As a result, CAs measured in Fig. 5(i) are higher than that in Fig. 5(h)\textsuperscript{[30]}.

4. Conclusion
In this paper, LIBT was successfully used to fabricate the "lotus effect" surface on superhydrophilic glass. The glass surface was roughened and coated by a thin layer of FEP in a single step, resulting in strong water repellence and extremely weak adhesion. It was proved that the larger the scanning interval was, much more apparent anisotropic wetting behaviors and much weaker hydrophobicity could be seen. Laser radiation provides a driving force for FEP transfer. However, XPS revealed that laser radiation also induces oxidation and defluorination, which are both adverse factors for wetting ability. Therefore, hydrophobic performance of the glass surface exhibited a nonlinear relationship with laser power. Anyway, for each scanning interval, there still exists an optimum laser-power window for superhydrophobicity. In addition, a combination of the Cassie and Wenzel models was proposed for explaining anisotropic wetting behaviors and adhesion modification. Due to its ability of large-scale fabrication with high-processing resolution, LIBT would be a promising method for fabricating functional surfaces with diverse wettability.

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References