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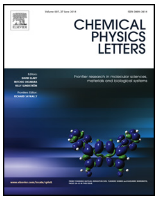

A facile method to fabricate superamphiphobic polytetrafluoroethylene surface by femtosecond laser pulses

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ABSTRACT

We report a simple method to fabricate superamphiphobic polytetrafluoroethylene (PTFE) surfaces by femtosecond laser direct irradiation. After femtosecond laser direct writing, a dual-scale composite structure combined a groove-like microstructure with a lamellar submicron structure forms on the PTFE surface, enhancing its hydrophobic properties with a contact angle increasing from 109° to 156.88°, as well as exhibiting transition from intrinsic oleophilicity to superoleophobicity. Meanwhile, the wettability of the surface can be tuned by changing the roughness and the interval between two adjacent micro-grooves. Furthermore, we also explain the relationship between the interval width and the contact angle using the Cassie–Baxter model.

1. Introduction

A superhydrophobic surface is characterized by a contact angle (CA) greater than 150° and a rolling angle typically smaller than 10°, which has several practical functions such as self-cleaning [1], non-fouling [2], drag reduction [3], spill-resistant protective wear [4], and chemical shielding [5]. Barthlott and Neinhuis [6] first reported that the self-cleaning lotus effect can be attributed to epicuticular wax crystalloids with a low surface energy and micro-nano dual-scale structures. According to the Wenzel model [7] and the Cassie–Baxter model [8], the wettability of surfaces is dominated by both the surface energy and the microscopic morphology; the hydrophobicity can be enhanced by lowering the surface energy and improving the roughness of surfaces, which applies to oleophobicity as well.

However, natural oleophobic surfaces are rare, and there are no known naturally occurring superoleophobic surfaces, because the surface tension values of oils are significantly lower than that of water [9]. Surfaces only by lowering the surface energy without being textured on flat substrates cannot achieve contact angle values larger than 130°. Therefore, various methods to fabricate rough surfaces with both low surface energy and micro-nano dual-scale composite structure to realize superhydrophobicity and superoleophobicity have been developed. To date, many methods have been proposed to control the surface morphology, such as surface modification [10–12], coating [13,14], electrospinning [15], nanostructure synthesis [16], etching [17], and lithography [18]. However, some of these texturing methods have obvious shortcomings, such as multiple steps, difficult operation, and long processing time.

PTFE is an artificial hydrophobic but oleophilic polymer and has thermal stability, chemical inertness, and low surface energy of 20 mN/m. Thus far, some researchers have paid great attention to the superhydrophobicity of PTFE surfaces. For example, Lau et al. [19] reported to create a superhydrophobic surface by growing a forest of nanotube pillars with a nonwetting PTFE coating approaching that of a perfect air–water interface with CA of 180°. Zhang et al. [20] proposed to change the density of the fibrous crystals through axial extension to achieve a superhydrophobic surface with a water CA of 165°. Daoud et al. [21] utilized pulsed laser deposition to deposit PTFE thin films on cellulosic cotton substrates to fabricate superhydrophobic PTFE-coated fibers. Kwong et al. [22] also obtained superhydrophobic PTFE thin films with high water CA of about 170° and the rolling angle smaller than 2° via pulsed laser deposition technique. Kawamura and Nakafuji [23] employed 10-ns laser pulses with 266 nm central wavelength to irradiate PTFE surface and obtained superhydrophobic PTEE surface with cotton-like micro structures. Recently, Liang

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et al. [24] studied robust non-wetting PTFE surfaces by femtosecond laser ablation, which exhibits a forest-like fiber entangled structure. Toosi et al. [25] investigated the influence of femtosecond laser irradiation process parameters, such as laser fluence, scanning speed and beam overlap, on the wettability of the micro/nano-patterned PTFE surface. Besides, some other papers are also involved with the research of laser micro manufacturing or/and superhydrophobic property of PTFE [26–32]. Although great achievements of fabricating or synthesizing superhydrophobic PTFE surface have been made, there are still few reports about achieving oleophobicity or superoleophobicity on PTFE surface, which is also very important in surface science, material science and biochemistry.

Therefore, we propose a simple method in our paper that utilizes a femtosecond laser to irradiate directly on a PTFE plate, which forms micro-nano dual-scale composite structure that plays a dominant role in realizing robust superamphiphobicity of PTFE surface. The femtosecond laser beam was focused on the PTFE surface for laser processing to enhance the surface roughness without additional surface treatment. The microscopic morphology of the laser-processed surface was scanned by scanning electron microscope (SEM), and the contact angles and rolling angles of oil and distilled water were measured. We compared the experimental result with the theoretical model and analyzed the relationship between the decrease of the contact angle and the increase of the micro-grooves interval.

2. Experiments

PTFE plates were purchased from Shangjiu Plastic Manufacturing Co. Ltd and were cut into small, 40 mm × 40 mm × 3 mm pieces. Before the experiment, the surfaces of the plates were polished, rinsed ultrasonically with ethanol for 5 min and dried in the air. Finally, the cleaned PTFE pieces were mounted on a three-dimensional (3D) linear translational stage.

The femtosecond laser pulses utilized for surface irradiation were produced by a 1-kHz regenerative amplified Ti:sapphire laser system with a central wavelength of 800 nm that emits 300-fs laser pulses. The horizontally polarized laser beam was focused by an objective lens (NA 0.3) onto the cleaned PTFE surface mounted on the 3D translational stage. The focused laser spot diameter on the PTFE surface was about 20 μm and the laser power used was 25 mW. By moving the 3D linear translational stage at a constant scanning speed of 3 mm/s in the *x*-direction and with a shift of the stage at a certain interval in the *y*-direction, several parallel micro-grooves in the *x*-direction on the PTFE surface were obtained [33]. This direct writing process produced an array of micro-grooves with an area of 5 mm × 5 mm on the PTFE surface. By tuning the intervals between two adjacent micro-grooves from 5 to 100 μm, a series of PTFE surfaces fabricated by femtosecond laser direct writing were obtained.

After fabricating the surfaces, we coated the surfaces with a thin chromium film to improve the electrical conductivity and used a JSM 6700F model scanning electron microscope (JEOL, Japan) at 20.0 kV to observe the microscopic surface morphology of samples. Static contact angles and rolling angles were measured with a contact angle meter (SL200B) by the sessile drop method. Micro-syringes were used to drop 5-μL distilled water droplets with surface tension of 72.8 mN/m and olive oil droplets with surface tension of 32 mN/m gently on the center of each plate surface. The images of droplets were captured with the system's charge-coupled device (CCD) camera. The Young–Laplace equation fitting (ADSA-P) [34], which can determine the contact angles from the shape of axisymmetric menisci (i.e., from sessile as well as pendant droplets) by fitting the experimental droplet profile to a theoretical one given by the Laplace equation of capillarity, was used to measure the contact angles formed at the liquid–solid interface.

3. Results and discussion

Superhydrophobicity and superoleophobicity are typically attributed to low surface energy and micro-nano composite morphology. The chemistry of the PTFE plate surface irradiated by laser was similar with the untreated one, and it is mainly the microscopic morphology of the treated PTFE surface rather than surface chemistry that accounts for the change in wettability after femtosecond laser manufacturing [25].

Figure 1 shows SEM images of the laser-processed PTFE surface. In Figure 1(a), one can see the treated PTFE surface with an array of parallel micro-scale groove-like structures and the dark untreated PTFE parts. Figure 1(b)–(f) show the magnified details of the fabricated PTFE surfaces with the interval widths ranging from 5 to 25 μm. One can see distinct micro-grooves structures with interval larger than 10 μm in Figure 1(d)–(f) which increase the roughness of the PTFE plate surface. The inset of Figure 1(f) shows the hierarchical structure between two adjacent micro-grooves which contains many lamellar structures with a thickness of dozens of nanometers and can dramatically increases the volume of trapping air. However, only blurry micro-grooves can be observed in Figure 1(c), in which an interval of 10 μm between two consecutive *x*-direction scans corresponds to an overlap of 50%. Also, in Figure 1(b), clear micro-grooves cannot be observed, only the stretches of porous PTFE microstructures can be seen due to a higher overlap of 75%. The forest of compact and entangled microstructures makes the surfaces in Figure 1(b) and (c) much rougher than the ones in Figure 1(d)–(f).

The contact angles and rolling angles of distilled water/oil droplets on the untreated/treated PTFE surfaces were measured to investigate the wettability of the surfaces. Figure 2 shows a comparison between side views of water/oil droplets on treated and untreated PTFE surfaces. The CA of 5-μL distilled water increases from 109° on the untreated PTFE plate surface (Figure 2(a)) to 156.88° at a micro-grooves interval width of 10 μm (Figure 2(b)) and its rolling angle was 4°. Even when the interval width increased up to 40 μm, such superhydrophobic surface (with a contact angle greater than 150° and a rolling angle smaller than 10°) could also be easily obtained. In Figure 2(c) and (d), one can see the CA of 5 μL oil droplet increases from 61° on the untreated PTFE surface to 153.35° at a micro-grooves interval width of 10 μm (the rolling angle was measured as 9°). In contrast to the previously untreated oleophilic surface, the fabricated rough PTFE surface here achieves superoleophobic property.

In the step of measuring contact angles, a water or oil droplet of small volume like 2 μL could not be easily dropped on the treated substrates with interval micro-grooves smaller than 10 μm. When the droplets' volumes were enlarged to 5 μL, they could be successfully dropped on the surfaces owing to gravity. However, when the interval between two adjacent micro-grooves decreased down to 5 μm, water or oil droplets could hardly be dropped on the surface due to repellency, which obviously exhibits the realization of superhydrophobicity and superoleophobicity of PTFE surfaces.

We not only enhanced the hydrophobic property but also realized the transition from oleophilicity to superoleophobicity of the PTFE surfaces. However, once the surfaces were fabricated micro-grooves with intervals larger than 10 μm, although we could still realize oleophobicity with relatively high CAs (for example 144.74° in Figure 5), small rolling angles of oil droplets could not be obtained due to the high viscosity and low surface tension (32 mN/m) of olive oil. As shown in Figure 2(e) and (f), when the plate with 15 μm